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Conversion of organic solid waste into energy and functional materials using biochar catalyst: Bibliometric analysis, research progress, and directions

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ABSTRACT

Much effort has been made to use biochar to catalyze organic solid waste conversion into value-added products. Biochar has a high specific surface area and abundant functional groups, making it a promising catalyst, but biochar is not used in industrial-scale applications. Presented here is a systematic literature review and bibliometric analysis of biochar-catalyzed solid waste research between 2000 and 2023 focused on the mechanisms involved in and factors affecting biochar catalytic performance during biomass and organic polymer conversion. In situ catalysis allows flexible and simple processes giving specific products but gives relatively poor conversion efficiencies. Catalytic conversion of organic solid waste by biochar has been a focus of research since 2006. A discussion of biochar catalysis applications, computational approaches, and sustainability is presented. The review indicates recent progress using biochars as catalysts for converting waste into valuable products and provides valuable insights that will advance environmental and waste management practices.

1. Introduction

There are many types of solid waste, including municipal waste (e.g., food waste, sludge, and food scraps), polymers (e.g., polypropylene, polyethylene, and polystyrene), medical waste (plastic products), and agricultural and forestry waste (e.g., rice husks and straw, peanut waste, and grass clippings). Solid waste is an important source of environmental pollution because of its complex composition and the large amounts produced [1]. The total volume of solid waste has been predicted to increase from 1.90×10^9 t in 2004 to $4.8 \times^9$ t by 2030 because of urbanization and rapid population growth, and the waste production growth rate is predicted to become higher than the population growth rate [2,3]. Polymer waste (including various types of waste plastic) is particularly problematic. Wang et al. predicted that 85% of marine litter will be plastic by 2040 and that 23×10^6–37×10^6 t of plastic per year will enter the marine environment [4]. Organic pollutants (e.g., polymers and biomass, which account for 44% of total solid waste [5]) are the most seriously polluting but recyclable types of solid waste. The value of such waste is not fully utilized. Current organic solid waste management practices are unsatisfactory. Traditional disposal methods such as recycling, incineration/combustion, and sending to landfill are generally inefficient, allow poor energy recovery, and cause secondary pollution. In contrast, catalytic conversion (e.g., catalytic pyrolysis, catalytic cracking [6,7], and catalytic carbonation) are very promising

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Table 1
Mechanisms involved in conversion of biomass and polymers by biochar (BC) catalysts.

Catalytic type	Waste type	Decomposition method	Reaction Process	Mode of action of the catalyst	Reaction sequence
In-situ catalysis	Polymers	Pyrolysis of long-chain hydrocarbons	The chain propagation process is dominated by the free radical mechanism, and the catalytic process is dominated by the carbon ion reaction mechanism.	Dominant carbon ion reaction, hydrogen transfer and co-cracking.	Pyrolysis of polymers and catalytic cracking of BCs occur simultaneously.
	Biomass	Low-temperature hydrolysis (90–260 ℃) High-temperature pyrolysis (>260 ℃)	Polysaccharides are converted to monosaccharides, dehydrated sugars, or small molecules (e.g., furans, ketones, aldehydes, alcohols) and catalyzed to olefins, aromatics, and gases.	Catalytic conversion reactions catalyzed by acidic sites on the surface, catalytic dehydration and decarbonization reactions of functional groups on the surface.	Hydrolysis/pyrolysis of biomass occurs simultaneously with the catalysis of BCs.
Ex-situ catalysis	Polymers	Pyrolysis of long-chain hydrocarbons	The chain propagation process is dominated by the free radical mechanism and the catalytic process is dominated by the carbon ion reaction mechanism.	Dominant carbon ion reaction, hydrogen transfer and co-cracking.	Free radical mechanism in polymer pyrolysis and biochar-catalyzed carbon ion reaction mechanism in sequential order.
	Biomass	High temperature pyrolysis (>200 ℃)	Polysaccharides are converted to dehydrated sugars or small molecules (e.g., furans, ketones, aldehydes, alcohols); transferred to the catalytic region for catalytic cleavage reactions.	Surface functional groups and acidic sites and metal sites catalyze dehydration, decarbonization, oligomerization or decarboxylation reactions.	Solid-gas heterogeneous reactions and gas-gas reactions.

methods for treating solid waste and cause little pollution. These techniques give good resource recovery rates and convert waste into value-added products.

Catalysts (e.g., metals and metal oxides) are crucial for converting organic solid waste because they improve the conversion rate and ensure that the desired products form. Commonly used catalysts (e.g., TiO_2, ZnO, and CdS) have a number of disadvantages, such as undergoing photolysis and releasing toxic metal ions [8]. Biochar, a carbon-based material, can be made from various feedstocks (raw materials) using a number of methods. The characteristics of biochar (e.g., pore structure, number of pores, and surface functional groups) are key to its catalytic activity. A good catalyst has a rich pore structure and abundant surface functional groups, and can be modified in various ways [9]. Biochar can be produced by thermochemically converting waste material, which allows good use of waste, promotes a circular economy and environmental sustainability [10], and decreases the effects of waste on terrestrial and aquatic organisms. Biochar can effectively catalyze the conversion of organic solid waste into biofuel/fuel, hydrogen, functional materials, aromatic compounds, and other value-added products, turning waste into treasure [11].

Biochar can degrade refractory organic contaminants through persistent free radicals generated during incomplete surface decomposition and electron transfer [12]. Adding biochar catalysts can decrease the concentrations of oxygenated components (e.g., acids) in bio-oil, increase the concentrations of target products (e.g., phenols), and improve selectivity. Adding biochar catalysts during the thermochemical conversion of biomass not only catalyzes pyrolytic volatilization (splitting the biomass into small gaseous molecules) but also acts as a source of carbon that participates in and facilitates water–gas reactions, and so effectively increases the H_2 and CO yields. Biochar can also participate in catalytic reformation of tar. Biochar catalysts are mainly modified by activating and doping functional groups. Biochar modifications can control the products and catalytic reformation processes by changing the specific surface area (SSA), porosity, and numbers and types of functional groups of the biochar. Improving the conditions for reactions between a biochar catalyst and solid waste increases the target product yield. The use of biochar to catalyze the conversion of solid waste into value-added products has recently become a popular research topic.

Uses of biochars as catalysts to convert solid waste into bio-oil and chemicals have been summarized in several recent reviews. For example, Xiong et al. [13] summarized the use of biochar to catalyze biodiesel production and synthesize chemicals from biomass. The focus was on only one type of solid waste, biomass, but multiple applications were described, although no attention was paid to the mechanisms and reaction processes involved in the catalytic conversion of solid waste by biochar. Li et al. [14] summarized the uses of biochar-based catalysts in lignocellulosic biomass pyrolysis but mostly focused on biochar formation and activation methods. Insufficient systematic assessments of the mechanisms involved in and factors affecting the use biochars as catalysts for the conversion of organic solid waste such as plastics and biomass have been performed. Importantly, solid waste conversion into functional materials is an important emerging topic but has been neglected in previous reviews. In this review, studies of the mechanisms involved in and factors affecting biochar-catalyzed conversion of organic solid waste between 2000 and 2023 are summarized and a bibliometric analysis of studies related to catalytic production of functional materials is performed. Publication trends, co-citations, categories, keywords, and clusters of similar publications relating to biochar-catalyzed conversion of solid waste into functional materials are analyzed, and keyword co-occurrence graphs analyzed using VOSviewer are used to provide new insights into catalytic conversion of organic solid waste.

2. Principles of biochar-catalyzed waste conversion

Waste can be converted into useful products using biochars as catalysts using two main processes: in situ catalysis in which the raw material is mixed with the catalyst before pyrolysis and ex situ catalysis in which pyrolysis gas is passed through a catalyst [15]. The catalyst is in close contact with the waste during in situ catalysis, so the catalytic sites are fully utilized and a good conversion efficiency is achieved. However, close contact has several drawbacks, including high energy consumption, low product selectivity, and contact with the catalyst becoming blocked by the material produced, and these limit the applications of close contact methods. The lack of direct contact with waste in ex situ catalysis allows great flexibility because the catalyst is not present during the initial waste pyrolysis stage and catalytic conversion can be performed under the most appropriate conditions. Ex situ catalysis avoids deactivation caused by direct contact between the catalyst and the reactants and allows the selective production of high quality bio-oil and the synthesis of a wide range of gases [16].

Reviewing recent waste-to-energy and functional material conversion studies indicated that biomass-like waste and polymeric materials are two types of waste particularly worth investigating. Different mechanisms are involved in in situ and ex situ catalysis. The mechanisms involved in conversion of waste using biochar catalysts are summarized in Table 1, and in the next section are discussed in depth in relation to the two perspectives and two types of raw materials mentioned above.

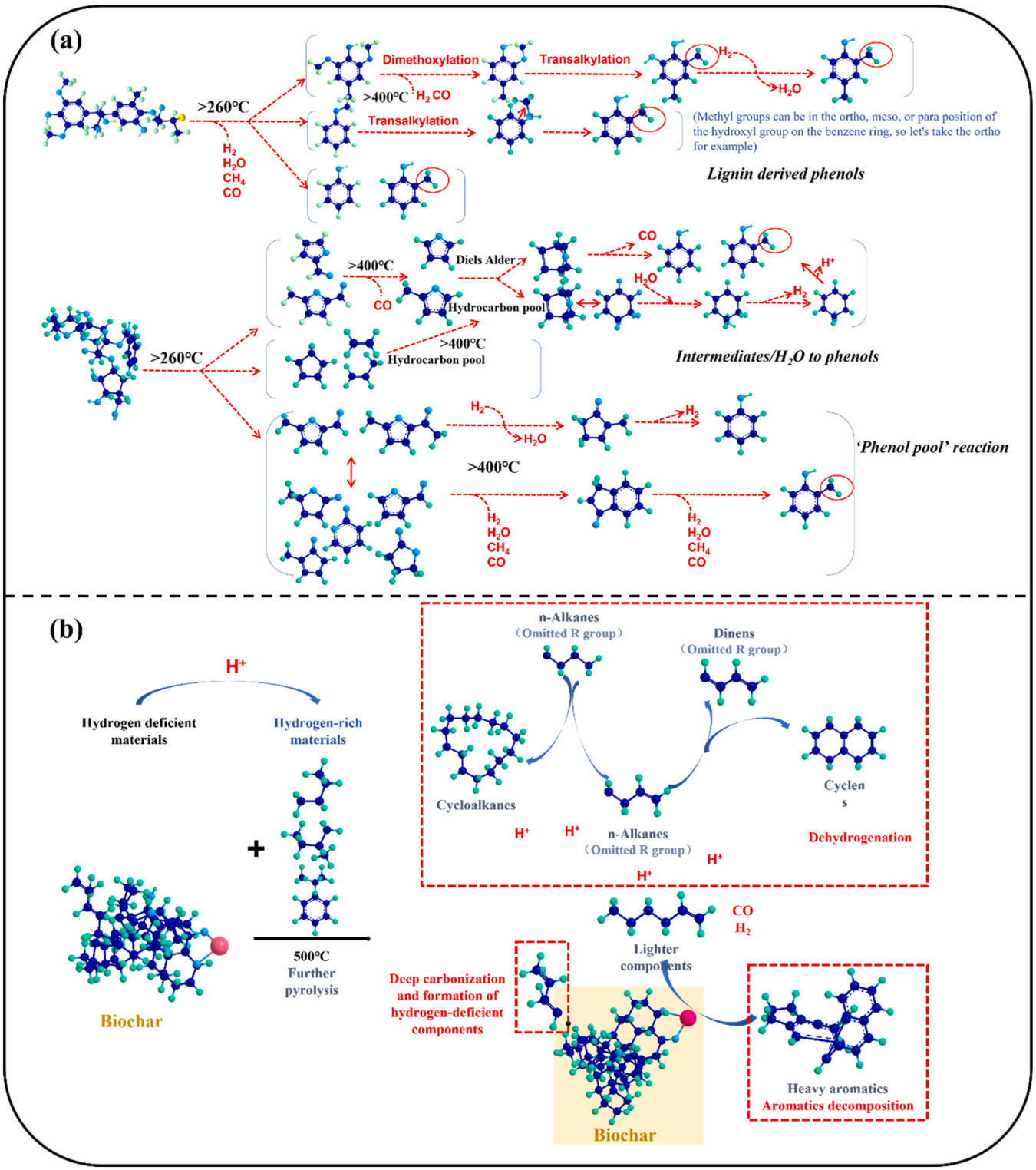

Fig. 1. Schematic diagram of the mechanisms involved in (a) biochar-catalyzed biomass conversion to give phenol [22] and (b) biochar-catalyzed in situ plastic conversion [1].

2.1. In situ waste conversion by biochar catalysts

2.1.1. Principles involved in situ conversion of biomass by biochar catalysts

Two main catalytic mechanisms are used to convert biomass and biomass-like waste into products: hydrolysis at low temperatures and catalytic pyrolysis at high temperatures. A schematic diagram of the mechanism involved in biochar-catalyzed biomass conversion to give phenol is shown in Fig. 1(a). Hydrolysis is generally performed at 90–260 °C. In the first step, polysaccharides in cellulose, hemicellulose, and lignin are converted into monosaccharides [17]. This involves converting dextran and xylan into glucose and xylose, respectively, with the Brønsted and/or Lewis acids on the biochar-based catalyst surfaces effectively acting as catalysts. A Brønsted acid can provide H^+ ions or form electron pair bonds during hydrolysis and this will lead to the

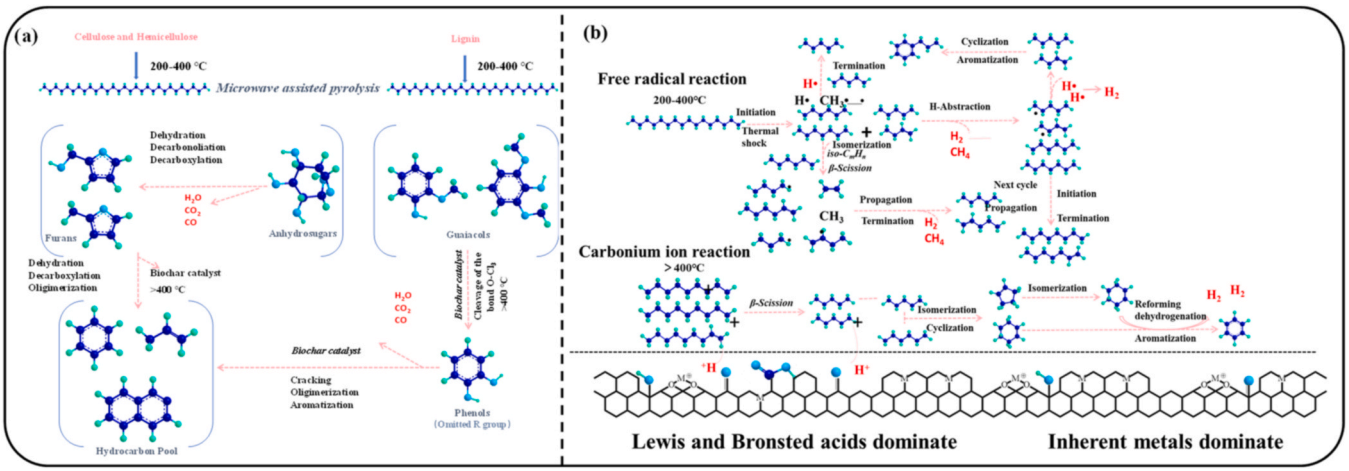

Fig. 2. Schematic diagrams of the reaction mechanisms involved in (a) ex situ catalytic pyrolysis of lignocellulosic biomass [24] and (b) pyrolytic conversion of polymers catalyzed by biochar [29].

glycosidic bonds in the polysaccharide being attacked and oxygen-containing moieties being converted into cyclic carbon ion moieties that can preferentially bind to OH^- ions to produce monosaccharides [18]. A Brønsted acid can also catalyze a Lewis acid to weaken the glycosidic bond by binding to glycosidic oxygen and promote monosaccharide formation [19]. The resulting monomeric aldoses can be converted into ketoses such as fructose and xylose through isomerization catalyzed by Brønsted or Lewis acids at 90–110 °C, the catalytic effect mainly involving critical hydrogen transfer from C_2 to C_1 [20]. Ketoses are then mediated by Brønsted acid catalysis at 120–200 °C to dehydrate to give chemicals such as 5-hydroxymethylfurfural and glyoxal [13]. Pyrolysis is usually carried out at > 400 °C. At such a high temperature, biomass is rapidly pyrolyzed and depolymerized to produce dehydrated sugars such as glucomannan and glucosone, which then decompose to a large number of small molecules (e.g., furans, ketones, aldehydes, and alcohols) through dehydration, decarbonization, and endothermic reforming reactions.

2.1.2. Principles involved in in situ polymer conversion catalyzed by biochar

The mechanisms involved in in situ catalysis of polymers are not as complex as the mechanisms involved in in situ catalysis of biomass, and most of the biochar catalysis effects on polymers occur during pyrolysis. During in situ catalysis, polymer pyrolysis and cracking catalyzed by biochar occur simultaneously. Long-chain hydrocarbons in polymers are rapidly pyrolyzed to give small hydrocarbon molecules at > 200 °C, then these hydrocarbons will be cleaved through thermal shock to give various free radicals, and chain propagation processes will be initiated. The main three stages in the free radical mechanism are chain initiation, propagation, and termination [6]. During the process, H-extraction reactions occur between radicals generated during pyrolysis and hydrocarbons to give H_2 and olefins [21]. H_2, CH_4, and olefins can also form through β-cracking of $C_nH_m\bullet$ radicals [22]. However, C–C bonds will readily be catalytically cleaved by biochar to give numerous short-chain hydrocarbons. Further pyrolysis of biochar will be promoted by the presence of polymers, and the interactions will initiate hydrogen transfer reactions in which hydrogen moves from hydrogen-rich materials (e.g., polyolefin chains) to hydrogen-deficient materials (e.g., the biochar). This leads to hydrogen being extracted from hydrogen-rich hydrocarbons to the carbon surfaces of the biochar and the dehydrogenation process being enhanced, increasing the olefin yield. Minerals/metals in biochar can also act as catalytic sites to produce H_2 and aromatic hydrocarbon compounds through isomerization and dehydrogenation reactions with the olefins generated through polymer cracking. This results in conversion of the products of polymer pyrolysis into more stable substances with higher calorific values [1]. The mechanism involved in in situ plastic conversion catalysis by biochar is shown schematically in Fig. 1(b).

2.2. Principles involved in ex situ waste conversion catalyzed by biochar

2.2.1. Principles involved in ex situ biomass conversion catalyzed by biochar

Ex situ hydrolytic catalysis is not possible at low temperatures but ex situ pyrolytic catalysis occurs at > 200 °C. Pyrolytic catalysis has two clearly divided parts, a pyrolysis zone and a catalytic zone and involves a series of heterogeneous solid–gas reactions and gas–gas reactions. Initially, pyrolysis of cellulose and hemicellulose in biomass at 200–400 °C gives small-molecule compounds such as aldehydes, ketones, acids, furans, and dehydrated sugars [23]. These small molecules are then transferred to the catalytic zone for cracking reactions involving biochar as a catalyst, and dehydration, decarbonization, or decarboxylation reactions occur to give smaller compounds such as furans and H_2. Next, intermediates such as furans undergo oligomerization and decarbonization reactions catalyzed by acidic sites on the biochar surfaces and are converted into olefins and aromatic hydrocarbons [24]. Water in the biomass may form superheated water during pyrolytic volatilization, which can increase the acidity of the system by reacting with functional groups on biochar surfaces, and this further facilitates the conversion of pyrolysis intermediates into product chemicals [25]. Lignin is one of the substances in biomass that is more difficult to decompose, and lignin decomposition requires a high temperature for a long time. The main product of lignin pyrolysis is guaiacol, which in turn cleaves and reacts with furan to give phenolic compounds. Guaiacol can also be cleaved through biochar catalysis to give phenolic compounds through O–CH_3 demethylation. This contributes to the production of aromatic hydrocarbons [26]. The main volatile gases produced are H_2, CO_2, CO, and CH_4. The proportions of H_2 and CO in syngas are markedly higher after than before catalysis, and this mainly occurs through two mechanisms. The mechanism involved in ex situ catalytic pyrolysis of lignocellulosic biomass is shown schematically in Fig. 2(a). The first step is characterized by H_2O and CO in the volatile fraction entering the biochar catalyst. Metal sites in the biochar trigger water–gas transfer reactions that lead to the production of H_2 [14]. The second step involves methane undergoing the dry reforming reaction, which decomposes CH_4 or causes CO_2 to react to produce H_2 and CO [27].

2.2.2. Principles involved in ex situ polymer conversion by biochar catalysts

The mechanisms involved in ex situ catalysis of polymers and in situ catalysis are similar, the main difference being a sequential difference

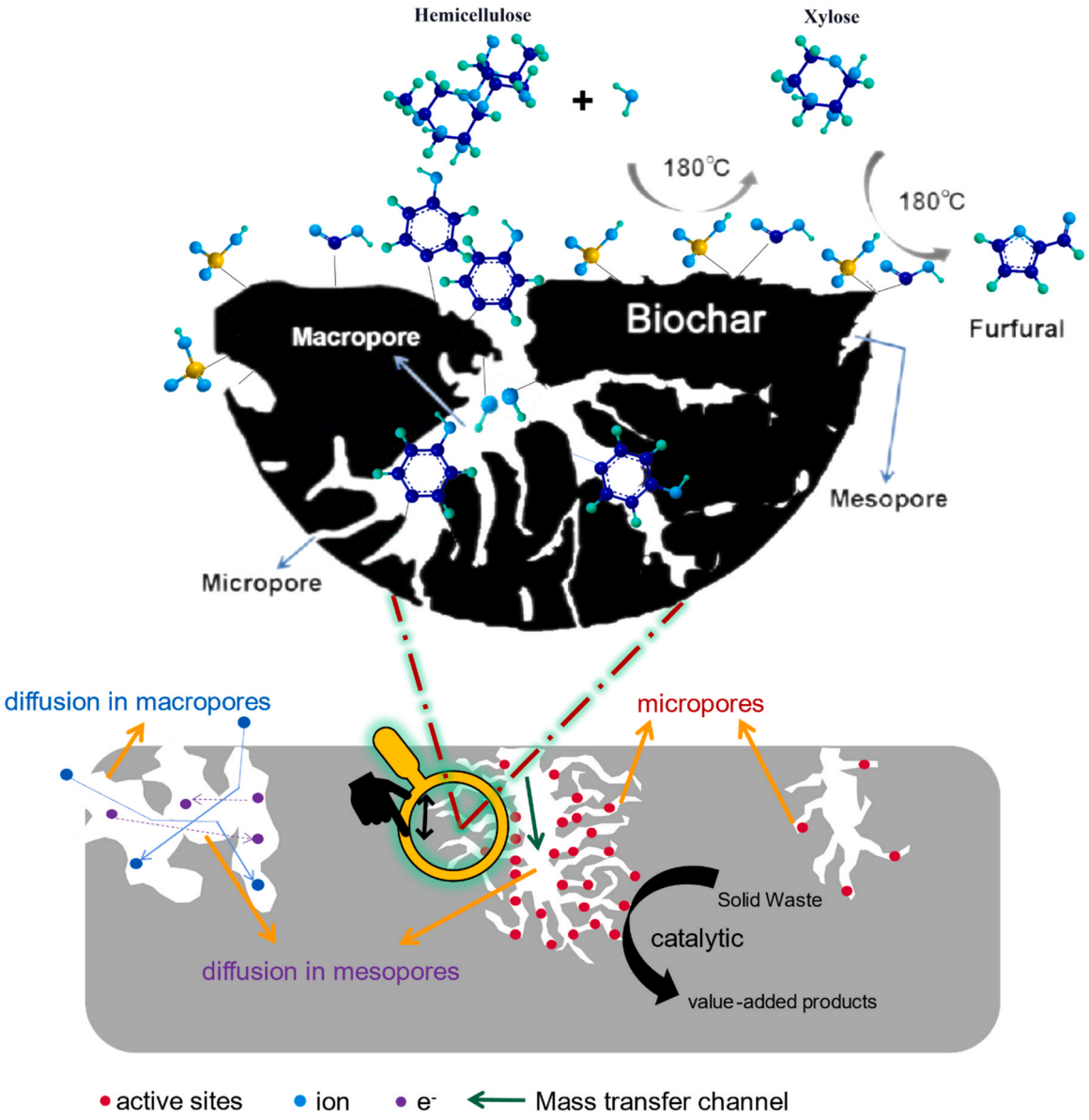

Fig. 3. Effects of the biochar structure on catalytic conversion of organic solid waste.

between free radical reactions during polymer pyrolysis and carbon ion reactions catalyzed by biochar. First, thermal decomposition of the polymer starts at 200 °C, when the free radical mechanism dominates [10]. Similar to the in situ mechanism, the radical reaction has three phases, chain initiation, propagation, and termination, but there are slight differences. In the initiation phase, pyrolysis generates large numbers of radicals such as H·, CH_3·, and C_mH_n·and propagates them outward. The propagation phase includes H-extraction, β-cleavage, and isomerization reactions and produces substances such as H_2, CH_4, olefins, and aromatic hydrocarbons. In the termination phase, the more stable carbon ions react with each other and newly generated radicals to produce H_2, CH_4, and short-chain olefins and alkanes [28]. Later, at higher temperatures (>400 °C), the catalytic reactions are dominated by carbon ion reactions. Initially, Brønsted and Lewis acids on the biochar surfaces dominate catalysis, provide H^+ ions, and act on C═C bilayers to produce the corresponding carbon ions. Pyrolytic conversion of polymers catalyzed by biochar occurs through the mechanism presented schematically in Fig. 2(b). Contact between carbon ions and alkanes tends to lead to isomerization reactions, which lead to the conversion of primary carbon ions into more stable secondary carbon ions. The long-chain carbon molecule ions subsequently undergo β-fission to give olefins and new carbon molecule ions or are converted into olefins through the recovery of acid sites by protons returning to the catalyst [29]. This results in numerous olefins being produced and then isomerization and cyclization to give cycloalkanes. These cycloalkanes are then catalyzed by the metal sites in the biochar to give large numbers of aromatic hydrocarbons and H_2 [30].

3. Effects of biochar properties on catalytic conversion

The biomass feedstock, preparation conditions, and modification methods strongly affect the properties of the biochar produced. Biochar with different physical and chemical properties have different characteristics in terms of the catalytic conversion of organic solid waste, reaction mechanisms that occur, and products. In this section, the effects of various biochar properties (SSA, porosity, surface charge, functional groups, and element composition) on catalytic conversion of organic solid waste and the mechanisms involved are described.

Table 2
Factors that affect the biochar structure and catalytic conversion of solid waste by the biochar.

Factors	Affected structures	Impact on catalytic conversion of solid waste	References
Pyrolysis Temperature	SSA and pore structure	The higher the SSA of biochar, the carbon nanotubes formed by catalytic conversion of plastics have more uniform diameter and complete bamboo structure	[10]
		SSA has a good catalytic effect for tar catalytic cracking	[35]
		The conversion of naphthalene is linearly correlated with the SSA of mesopores and micropores of biochar	[36]
Feedstocks	SSA and pore structure Pore structures	Catalytic conversion of low-density polyethylene and lignocellulosic biomass by corn stover biochar facilitates H_2 production (72 vol%, 650 °C, biochar/feedstock = 4)	[11]
		Sludge biochar catalytic conversion of plastics favors monocyclic aromatic hydrocarbon production at 600 °C (75.3%) and bicyclic aromatic hydrocarbon production at 800 °C (64.4%)	[56]
Chemical modification	Carbon deposition leads to lower SSA	After coking of the active sites in the micropores, the decomposition of toluene results in the generation of more stable benzene and reduction of the overall tar conversion	[57]
	Increased pore structure by metal salt and acid-base modification	SSA of $ZnCl_2$/biochar increased to 1032 m^2/g, promoting the conversion of plastics to aromatic compounds by pyrolysis	[50]
		Activation of KOH increased the SSA of biochar to 1286.44 m^2/g and promoted the catalytic pyrolysis of biomass to liquid oil (38 wt%) and biochar (22 wt%)	[49]

3.1. Influences of the porous structure of biochar on thermocatalytic conversion of organic solid waste

Biochar catalysts contain the main sites at which organic solid waste and the products adsorb and undergo catalytic transformations [31]. Biochars usually have high SSAs and many pores [32], mainly because of the structure of the original biomass that was pyrolytically carbonized, which involves processes such as dehydration, volatilization of active substances, fracturing, and collapse [33]. After pyrolysis, the "skeleton" and pore structure mainly consist of aromatic compounds [34]. As shown in Fig. 3, adsorption and catalysis of organic solid waste by biochar are controlled by the biochar pore structure, and different pore structures give different effects. Fuentes-Cano et al. found that N_2-diluted steam-activated biochar catalyzed tar cracking well and that more naphthalene was converted as the surface area of the pores in the biochar increased. This was because the rich pore structure promoted the generation of oxygen-containing functional groups, which enhanced catalytic conversion by the biochar and facilitated the conversion of tar into the small molecule product naphthalene [35]. Ravennni et al. found that micropore-rich biochar also catalytically converted tar into naphthalene well because the microporous structure contained many active deposition sites and effectively prevented the active sites from being blocked through coking [36]. A macroporous structure means ions have very short diffusion distances during the catalytic conversion process, mesopores decrease resistance to electrons, and micropores give a high adsorption capacity, meaning large amounts of the organic solid waste and products can adsorb to the catalytic sites and therefore the catalytic reaction will be completed quickly. Overall, performance is mainly improved by increasing the SSA and porosity of the biochar to expose more active sites. The adsorption capacity of biochar and the number of catalytically active sites in the biochar can be altered by changing the SSA and porosity [37], and this will affect the catalytic conversion process and the products [38]. At an appropriate pyrolysis temperature, an excellent electron transfer efficiency can be maintained but the a high SSA and a high degree of porosity will mean many catalytically active sites are exposed and the catalytic conversion performance will be optimized [39,40].

3.1.1. Effects of the pyrolysis temperature on the porous structure and catalytic activity of biochar

Catalytic conversion of solid waste can be affected by changing the porous structure of the biochar. The pyrolysis temperature, biomass feedstock, and ash content are the main factors that affect the porous structure of the biochar produced. Biochar generally has a SSA of 3.3–640 m^2/g [41], and the SSA increases as the pyrolysis temperature increases within a certain temperature range [42]. The formation of biochar pores is affected by the temperature used to thermally decompose the biomass. At lower temperatures (~400 °C), volatile compounds, tar, and other substances may clog the pores and decrease the SSA [43]. In contrast, increasing the temperature causes these substances to break down into volatile gases and be released, allowing the pores to contract, increasing the number of pores and creating more microporous structures, which ultimately increases the SSA [44]. However, there is a critical temperature (~800 °C) above which the SSA decreases as the temperature increases, probably because of the formation of carbon deposits from certain volatile organic compounds at active sites [44,45]. Such carbon deposits are responsible for decreases in both the catalytic activity and SSA of the biochar. Carbon deposition will destroy the microporous structure of the biochar and therefore decrease the catalytic activity. The carbon deposition and decomposition rates are therefore critical factors affecting the catalytic capacity of the biochar. If the deposition rate is lower than the decomposition rate, the biochar will maintain its original activity, otherwise the biochar will gradually lose its activity. The temperature is one of the factors that regulates the carbon deposition and decomposition rates. For example, the carbon decomposition rate will be higher than the carbon deposition rate at high temperatures (>700 °C) when CO_2 and H_2O are present, meaning the yields of stable gases (H_2, CO, and a small amount of CH_4) during the catalytic conversion process will increase [16].

3.1.2. Effects of the biomass feedstock on the porous structure and catalytic activity of biochar

The biomass feedstock affects the porous structure of biochar. Cellulosic biomass is generally rich in internal pores, and biochar produced by pyrolyzing and carbonizing cellulosic biomass retains the original fine pore structure and has a high SSA. The pore structure of non-cellulosic biomass is relatively simple, so the SSA is lower for biochar produced from non-cellulosic biomass than cellulosic biomass [46]. For example, rice straw biochar has an SSA of 285 m^2/g [47] but sewage sludge biochar has an SSA of 47 m^2/g [48]. The ash content also affects the SSA of biochar. The ash content usually increases as the pyrolysis temperature increases, and ash may occupy biochar pores and therefore decrease the SSA and porosity of the biochar [49].

3.1.3. Effects of chemical modifications on the porous structure and catalytic activity of biochar

Chemical modifications, including metal modifications and acid–base modifications, can affect the porous structure of biochar. Impregnating $ZnCl_2$ into biochar was found to increase the surface area of and number of micropores in biochar by Sun et al. [50]. This enhanced catalytic conversion of pyrolyzed plastic to give aromatic compounds. Strong catalytic selectivity for aromatic compounds was found at 500 °C, and the aromatic compound content of the produce was 47.5%. Bicyclic aromatic compounds were significantly enriched in the oil produced, contributing 90.7% of the total aromatic compounds. The main component was 1,3-diphenyl propane, which contributed 19.4% of

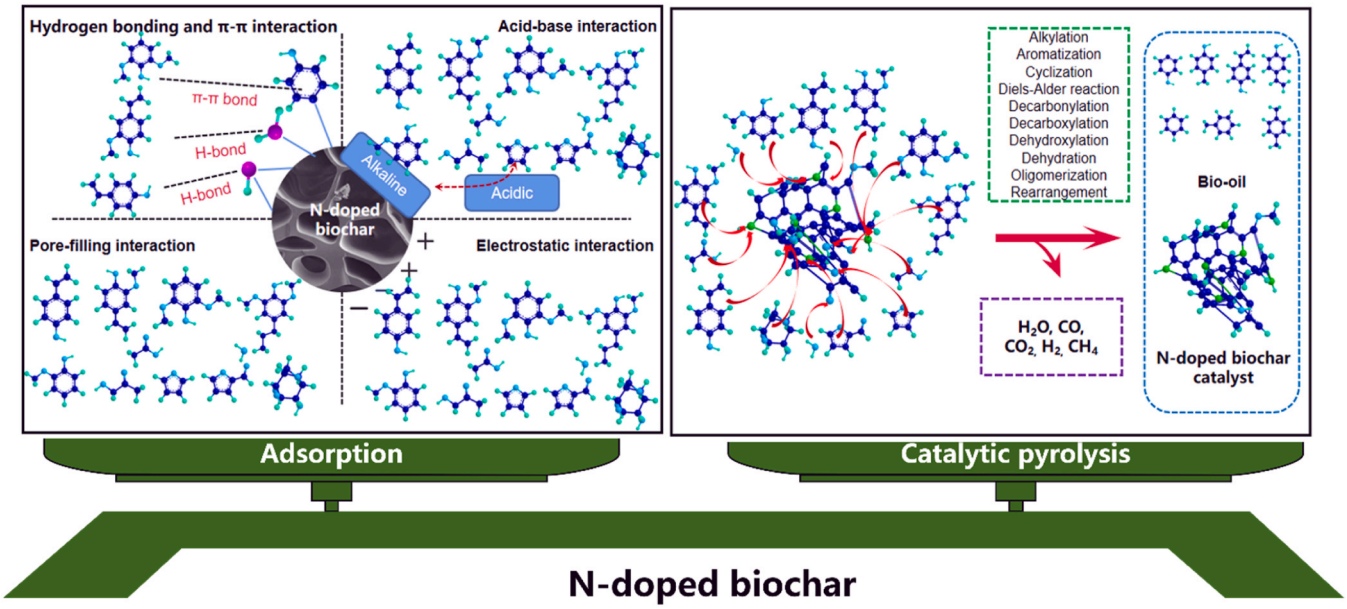

Fig. 4. Possible catalytic mechanism for N-doped biochar (the molecular formulae in the figure are taken from references [65] and [68]).

the mass of oil produced [50]. Yang et al. [51] found that activation with KOH increased the biochar SSA from 19.16 to 1286.44 m^2/g and the porosity from 0.07 to 0.59 m^3/g. The liquid yield was 38% by weight lower, the gas yield was 44% by weight higher, and the solid yield was not markedly different when KOH-activated biochar was used to catalyze in situ pyrolysis of bamboo chips than when non-activated biochar was used to catalyze in situ pyrolysis of bamboo chips. This may have been caused by the high SSA of the KOH-modified biochar providing a large surface area for the catalytic conversion of the bamboo chip biomass and increasing contact between volatile compounds produced during pyrolysis with active sites and allowing large volatile molecules to be converted into small gaseous molecules [51].

In conclusion, as shown in Table 2, many factors, including the biomass feedstock, preparation conditions, and chemical modifications, strongly affect the porous structure of biochar and therefore affect the catalytic conversion of organic solid waste. It is possible to produce biochar catalysts with unique features that can effectively catalyze the conversion of organic solid waste into high-value products and functional materials by optimizing the conditions mentioned above.

3.2. *Influence of functional groups in biochar on thermocatalytic conversion of organic solid waste*

Active sites on biochar are important to the catalytic conversion of waste and polymers and are closely related to the functional groups in biochar. Functional groups on biochar surfaces can have various acid–base properties and can be active sites for catalytic reactions [52]. For example, oxygen-containing groups (e.g., –OH and –COOH) are weakly acidic but N-containing groups (e.g., pyridinic-N, pyrrolic-N, quaternary-N, and pyridone-N-oxide) are basic [53]. Many acidic intermediates and carbonyl groups are produced during biomass pyrolysis, and N-containing functional groups will adsorb these substances well and promote pyrolysis reactions [54]. Fourier-transform infrared spectrometry, Boehm titration, and other methods have been used to characterize biochar before and after catalytic thermochemical reactions to determine whether functional groups participated in the thermochemical transformations, and the –COOH, C═O, –OH, and other functional group contents of biochar were found to have been changed by the reactions [55].

Various activation techniques have been developed to improve biochar catalytic efficiency and stability. Acid activation [58], alkali activation [59], plasma activation, and gas activation [60] can increase the functionalities of functional groups by increasing the numbers and types of functional groups and therefore increasing the degree of catalytic conversion [61]. Generally, increasing the number of functional groups improves catalytic conversion. Activation increased the number of oxygen-containing functional groups in biochar activated by H_2O (mainly C–O structures in aromatic groups), and these changes enhanced tar steam reformation [62]. In the whole process, the catalyst activity decreased as the number of C–O groups decreased, so it was concluded that oxygen-containing functional groups played important roles in the reactions. SO_3H-functionalized acid biochar produced from wood waste has been used to hydrolyze maltose to glucose at 140–160 °C and dehydrate fructose to 5-hydroxymethylfurfural at 160–180 °C [63]. Synergistic effects between –SO_3H groups and O-containing acidic groups (e.g., –OH and –COOH groups) may make the catalyst more polar and able to adsorb substrates, and –SO_3H groups may act as effective active sites for hydrolyzing adsorbed substrates. Such biochar catalysts with high Brønsted acidities and adsorption abilities actively hydrolyzed maltose and gave a glucose yield of 85%.

Chemically introducing heteroatoms (e.g., N, P, S, and Cl) can change the structure of a catalyst surface and therefore affect catalysis and selectivity of pyrolysis products. Chang et al. used HCl and $MnCl_2$ to modify peanut shell biochar and studied the effects on the pyrolysis product characteristics [64]. The results indicated that HCl-modification increased the number of oxygen-containing groups in the biochar, promoted uniform dispersion of active metal sites, and improved selectivity for phenols but was not conducive to H_2 formation. Modifying biochar with both HCl and $MnCl_2$ promoted lignin cracking and produced more phenols. Chen et al. used N-doped biochar to catalyze bamboo waste pyrolysis to produce phenol and found that N-doping biochar improved the bio-oil quality through synergism between adsorption of nitrogen-containing alkaline groups and catalytic conversion of oxygen-containing groups (as shown in Fig. 4) [65]. The roles played by N-containing functional groups in the catalytic process include breaking β-O-4 bonds and promoting –O–CH_3 cleavage [66] to promote phenol intermediate formation, which promotes reactions between the intermediates and H donors generated through hemicellulose and cellulose decomposition to give more phenols [67].

The reactions are not independent but interactive. Alkali and alkaline earth metals (AAEMs) can increase the numbers of hydroxyl, carboxyl, and other oxygen-containing functional groups on biochar

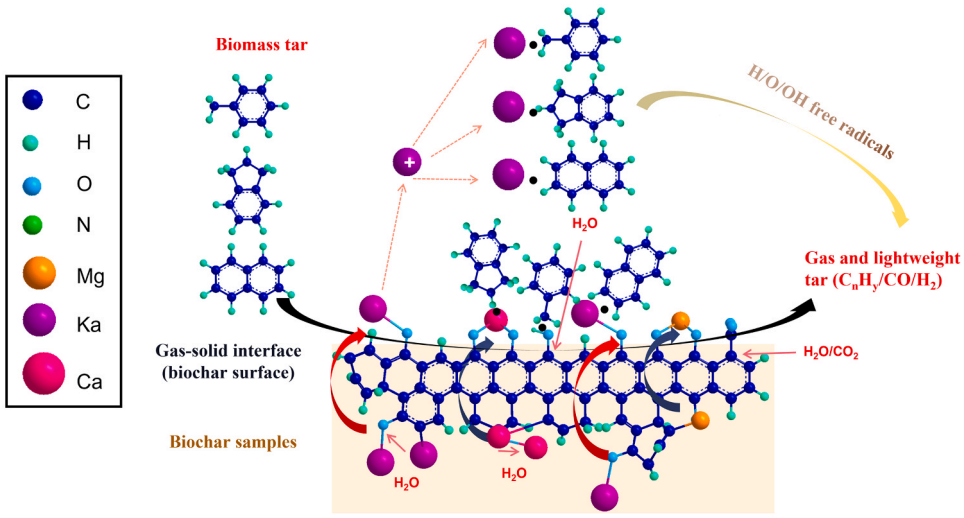

Fig. 5. Heterogeneous conversion mechanism involved in biomass tar reformation by biochar in the presence of H_2O and CO_2 at 800 °C [77].

surfaces [69,70] by, for example, increasing the H_2O adsorption capacity, which increases the number of hydroxyl groups on the biochar surfaces [71]. The presence of surface functional groups can affect the catalytic performances of AAEMs through charge transfer [59]. AAEMs and oxygen-containing functional groups promote interactions between volatile compounds and biochar and increase the numbers of lattice defects in the biochar, which promote continuous conversion of volatile organic compounds [72]. Functional groups such as hydroxyl and aldehyde can also form complexes with metals and induce pyrolysis dehydration.

In summary, the functional groups on biochar play important roles in catalytic conversion and increasing the number of functional groups will increase the reaction rate. However, the effects of different functional groups on the catalytic performance have not been systematically studied. Therefore, in addition to developing techniques to increase the numbers and variety of functional groups it is necessary to systematically study the mechanisms through which functional groups are involved in catalytic conversion to improve our understanding of the whole waste conversion system.

3.3. Influences of metals in biochar on thermocatalytic conversion of organic solid waste

Biochar can contain various elements because of the wide range of raw materials from which biochar can be prepared and the variety of compounds the raw materials can contain [73]. The organic components of biochar mainly contain C, H, and O, and the main inorganic components are AAEMs such as K, Ca, Na, and Si. Some types of modified biochar also contain transition metals (e.g., Fe, Mn, Co, and Ni) and noble metals (e.g., Pd, Au, Ru, and Pt) [74]. AAEMs, transition metals, and noble metals can affect the biochar SSA, porosity, and functional groups and also act as active sites during catalysis by the biochar or modified biochar [60].

Some researchers treated biochar with acid to remove AAEMs to allow the roles of AAEMs to be assessed, and this decreased the hydrogen yield by 19%, indicating the importance of AAEMs to catalysis by biochar [71]. During catalysis, AAEMs act as active sites that convert chemically adsorbed tar fragments into lighter components [6]. The roles of K and Ca (AAEMs commonly found in biochar) in catalytic tar reformation by biochar were investigated using rice husks with different loading states in a two-stage reactor [75]. The presence of K and Ca active sites promoted the generation of reactive intermediates (C–O bonds and C–O–K/Ca), which facilitated interactions between tar and the biochar. Fu et al. studied catalysis of lignite pyrolysis products by biochar and found that the light tar content increased as the N and S contents of the tar decreased [76]. K, Mg, Na, and other elements played important roles in catalyzing tar reformation. The heterogeneous conversion mechanism involved in biomass tar reformation catalyzed by biochar is shown in Fig. 5.

Metals have been attached to biochar surfaces as neutral atoms or metal oxides, and the catalytic performances of the modified biochars were mainly related to the presence of metal oxides and the porous biochar structures [78]. Adding Al effectively promoted the formation of phenolic substances during biomass conversion. Different metals have different catalytic effects. Ni gives a high hydrogenation activity and alloying efficiency, is relatively cheap, and gives excellent C–C, C–O, and C–H fracturing properties [79]. Biochar modified with Ni has a high catalytic activity for and is stable during hydrodeoxidation. Therefore, adding Ni promotes hydrodeoxidation and significantly decreases the oxygen-containing compound content and increases the aromatic compound content. Wang et al. fabricated a bimetallic Ni–Mo_2C/C catalyst through one-pot pyrolysis of sawdust with metal salts to create biochar with well-dispersed Ni that would be stable during the catalysis of lignin hydrogenation [80]. The combination of Ni and Mo_2C with strong metal-biochar interactions and graphitized biochar facilitated electron transfer and allowed catalytic hydrogenation of lignin with a high phenolic product yield. Metallic Fe has been found to be actively involved in C–C and C–H bond breaking, which facilitates aromatic hydrocarbon destruction [81].

Noble metals (Au, Ag, Pt, and Pd) do not rust or corrode as readily as other metals (e.g., Cu, Zn, Al, and Ni) but are very expensive. Adding noble metals improves the bio-oil hydrodeoxygenation and aromatization catalytic performance, so decreases the oxygen content during pyrolysis [82]. Biochar has been modified so that Pd and Lewis acid metal oxides (ZrO_2, WO_x, and MoO_3) acted as secondary active metal sites for lignin hydrogenolysis [83]. The results indicated that the modified catalyst could effectively produce C_9 phenol monomers during lignin biorefining. Various elements in biochar play important roles in catalytic conversion, especially in tar reforming, because the metals can act as active sites and promote reactions. It is clear that elements in biochar are involved in catalysis, but more research is required. We need to better understand interactions between metals and biochar and the influences of metals on the catalytic properties of biochar to allow new methods for using biochar to be developed.

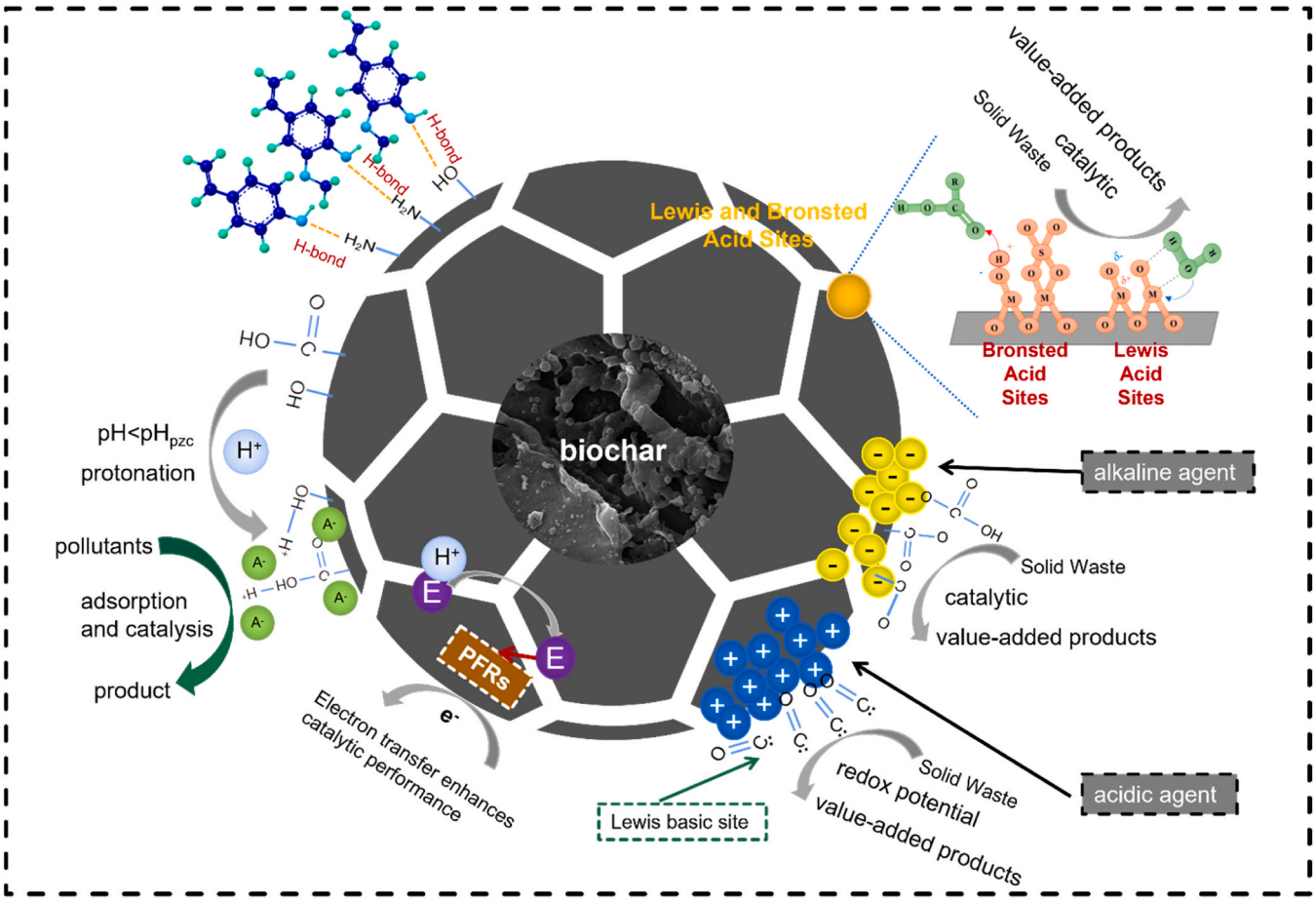

Fig. 6. Effects of the biochar surface charge on catalytic conversion of organic solid waste.

3.4. Influence of biochar surface charge on low-temperature catalytic conversion of organic solid waste

Biochar can mitigate water and soil pollution by catalyzing conversion of organic pollutants at low temperatures, and adding biochar is a cheap way of remediating polluted environmental media because of the powerful surface charge transfer that can occur. Interactions between biochar and both organic solid waste and pyrolysis intermediates are strongly affected by the biochar surface charge. The mechanisms involved in the effects of the biochar surface charge on catalytic conversion are shown in Fig. 6. The biochar surface charge is affected by the pH of the solution [84]. Negatively charged pollutants are electrostatically adsorbed by positively charged functional groups ($–OH^{2+}$ and $–COOH^{2+}$) on biochar that form through protonation reactions with surface oxygen-containing functional groups (–COOH and –OH with H^+) when the pH is below the equipotential point (pH_{pzc}) of the biochar. In contrast, negatively charged biochar surfaces can effectively adsorb positively charged pollutants at pH values higher than the pH_{pzc} of the biochar. Electrostatic adsorption allows pollutants to accumulate on the biochar surfaces, which improves contact between the pollutants and the active catalytic sites. This accelerates catalytic conversion of organic solid waste.

Pollutants become chemically adsorbed to active sites on biochar surfaces, and this is the first step of a catalytic reaction. Biochar acid–base sites are strongly affected by randomly oriented polyaromatic clusters, heteroatom surface functional groups, and minerals. Few studies of active sites on biochar surfaces have been performed. The active sites are often separated into Brønsted acid sites and Lewis acid sites. On biochar surfaces, highly polar hydroxyl groups may create Brønsted acid sites, which are proton donors. Brønsted acid sites can also be produced by the substitution of cations with lower valence charges because the net proton balance on the oxide-based catalyst becomes negative. Lewis acid sites are surface groups on biochar that can accept external electron pairs. Lewis acid sites form through coordinative unsaturation of the cation sites. Most such sites positively affect adsorption and catalysis by biochar [85].

The surface charge of biochar is affected by the temperature, oxygen-containing functional groups, degree of graphitization, hydrogen bonding, and ash content. The total number and density of oxygen-containing functional groups (e.g., alcohols, phenolic hydroxyl groups, hydroxyl groups, and carboxyl groups) decreases when the pyrolysis temperature increases, meaning the negative charge on the biochar surface decreases because hydroxyl and carboxyl groups are key to the surface charge of biochar [86]. Different functional groups on biochar surfaces (e.g., –OH, –COOH, O atoms in –C═O, and N atoms in $–NH_2$) can form hydrogen bonds with H in H_2O and therefore affect the zeta potential of biochar. Some surface charges generated through the polarization of bonds are neutralized by the formation of hydrogen bonds. Aromatic structures in biochar become more common as the pyrolysis temperature increases, leading to hydrogen bonds forming between π-bonds and H_2O. This neutralizes the surface charge generated by polarization and therefore increases the surface charge of the biochar. The deprotonated surface charge contributes to electron transfer by persistent free radicals on the biochar surfaces, which can improve the catalytic conversion performance of the biochar [87].

The graphitized structure of biochar means that π–π electron donors–acceptors can interact with organic polymers (organic solid waste). Biochar has excellent electron transfer properties because of extensive conjugation of sp^2 hybridized carbon atoms [88]. The catalytic activity of biochar can be effectively influenced by sp^2/sp^3

hybridization. First, promotion of internal transfer of electrons from an sp^3 carbon (donor) to an sp^2 carbon (acceptor) can cause external transfer of electrons from the carbon configuration that forms to a species actively involved in oxidation [89]. The graphitized structure becomes less stable by the formation of defect sites (e.g., edge defects, vacancies, and curvature), which improves the performance of the defective biocarbon as an electron donor. The graphene-like structure is generally a layer of carbon formed by three electrons in a carbon atom forming covalent bonds with three adjacent carbon atoms. The fourth valence electron forms a π-bond, so its movement is not restricted by the carbon structure because it is in a half-full orbit [90]. The delocalized π-electrons can migrate and form dangling σ-bonded states at the edges and defects because of the missing carbon atoms at these positions. Dangling σ-bonds with delocalized π-electrons at the defects can accelerate electron transfer at the edge carbon atoms, so catalytic reactions can occur at these sites.

In conclusion, the temperature, solution pH, and biochar factors (polarity and hydrogen bonding) affect the biochar surface charge, which in turn will affect the catalytic conversion performance of the biochar. Little research into how the feedstock affects the biochar surface charge has been performed. Further investigation is needed on the effects of the biochar surface charge on catalytic conversion reactions at high temperatures from a pyrolysis/gasification perspective and the quantitative relationship between these effects and the ability of biochar to catalyze organic solid waste conversion.

3.5. Influences of other factors on the catalytic conversion of organic solid waste by biochar

Some other factors, such as the biochar formation method and structural defects, also affect the organic solid waste catalytic conversion performance [58]. Feedstock can be converted into biochar by performing carbonization processes such as pyrolysis [91], gasification, and hydrothermal carbonization [92]. Pyrolysis is commonly used because it requires simple equipment, is a mature technique, and is cheap. Biochar yields are usually lower for gasification than pyrolysis because the gaseous products are the target products of the gasification process [85]. The carbon content is higher for biochar produced by hydrothermal carbonization than for biochar produced using dry processes, and hydrochar surfaces have high degrees of aromatization and large numbers of oxygen-containing moieties [93]. This is conducive to catalytic conversion of organic solid waste, which is worth exploring. Biochar is not perfect, and defects in the graphene-like structures have been found to catalyze tar cracking reactions [94], so attention needs to paid to biochar defects.

4. Bibliometric analysis of the use of biochar and modified biochar to catalyze organic solid waste conversion

The summary of research into the mechanisms involved in catalytic waste conversion by biochar above is mainly presented to give an overview of the current situation and areas in which research is deficient. Previously identified mechanisms have been described in some detail, but catalytic waste conversion by biochar remains poorly understood overall, making it difficult to identify necessary future research. Bibliometrics can be used to analyze development of the literature, numbers of publications, research hotspots, research methods, and author distributions in a research field at the macro level and to capture networks, structures, interactions, crossover, evolution, and other aspects of a research field to allow future development of the research field to be predicted. We therefore performed a bibliometric analysis of research into catalytic conversion of biomass using biochar to identify reliable suggestions for future research.

4.1. Data collection and methods

The Web of Science Core Collection and Scopus databases were used to provide data for the bibliometric analysis of research related to the catalytic conversion of waste by biochar. The information was collected on 10 January 2023. We used the search terms “biochar” OR “polymer” OR “catalysis” and the period 2000–2023, but few documents were identified and these were not strongly relevant to the target research. The keywords were therefore expanded and divided into three categories. For example, keywords related to biochar included biochar, manure, straw, biomass, agricultural and forestry waste, biomass carbon, electronic waste char, fertilizer, lignin, and biocharcoal. Keywords related to waste included polymer, polymer composite, plastics, fibers, adhesive, polyethylene, polypropylene, polystyrene, polycarbonate, rubber substances, polymers, compounds, adhesives, conjugated polymers, terephthalates, polyvinyl chloride, mixed polymers, waste materials, solid waste, fly ash, waste incineration bottom ash, waste oil, sludge, industrial waste products, waste and slag, agricultural waste, hazardous waste, off-gas substances, municipal waste, non-ferrous metal slag, solid particles, salt, blast furnace slag, gypsum waste, and cinder. Keywords related to catalytic conversion included functional materials, metal functional materials, inorganic non-metallic functional materials, organic functional materials, composite functional materials, transformation, catalysis, recovery, upcycling, utilization, use, reforming, green catalysts, novel catalyst, production, catalysis, convert, gasification, pyrolysis, carbonization, and liquefaction. A topic search was performed using these three keyword groups. Too few relevant documents were published before 2000, so the period 2000–2023 was used to ensure that sufficient relevant publications were identified. After cursory screening and duplicate data removal, 626 articles were selected for bibliometric analysis and processed using CiteSpace V. 5.7. R5. VOSviewer software, CiteSpace software, and bibliometrix software were used to visualize the data. The methods are described in detail in Supporting Information, Section 1.1.

4.2. Results and discussion

4.2.1. Analysis of publication, cooperation, and co-citation trends relating to research into catalytic solid waste conversion by biochar

Collaboration and co-citation analyses indicated that the number of publications increased faster after than before 2015 and that China, the United States, India, South Korea, and Germany were the leading countries in this research field (Fig. S1). Country and collaboration analysis (Fig. S2a) indicated that the earliest research was performed in the United States and the most papers were published by researchers from China. Researchers in China and the United States have been at the forefront of this research field in recent years and have collaborated with researchers from many other countries. Relevant research started to be performed in most countries in 2006. The number of publications by Asian researchers and the amounts of research performed in Asia has been increasing in recent years. This is related to large amounts of raw materials for producing biochar and large amounts of waste materials being available in China and India. Using biochar to catalyze waste conversion in efficient and environmentally benign ways has become a topical issue in Asian countries. The upward trend in the number of publications related to biochar-catalyzed organic solid waste conversion indicates that research in this field remains of great interest around the world and deserves further study. The number of publications has increased particularly strongly since 2019, and research has become focused on improving the catalytic conversion capacity of modified biochar and co-pyrolysis of biochar and organic solid waste to generate clean fuels and functional materials.

Research into biochar-catalyzed waste conversion has been published in a wide range of journals. Most attention has been paid to the processes involved in catalytic conversion of waste to energy and the characteristics of biochar catalysts. Bioresource Technology is the most

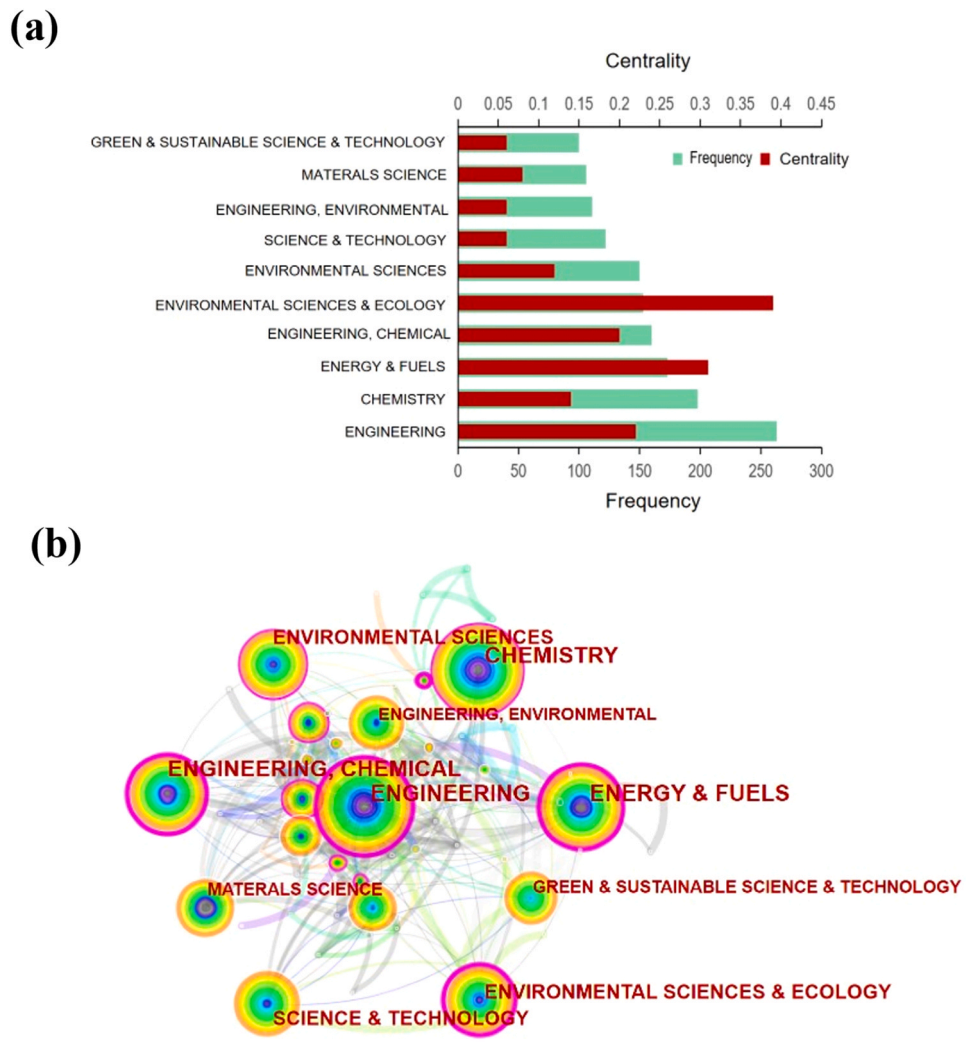

Fig. 7. (a) Frequency and centrality-based chart and (b) co-occurrence network graph for categories. In part b, the larger the node, the more frequent the category. The closer the central color of the node is to gray, the earlier the word appeared.

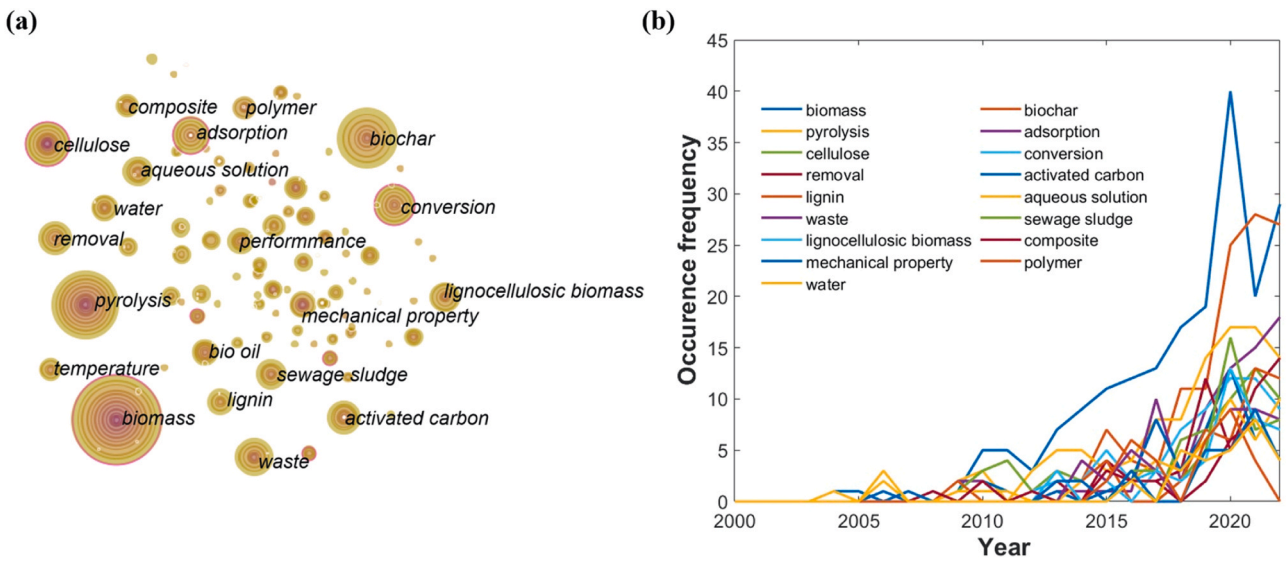

Fig. 8. Co-occurrence network diagram and (b) trend diagram for keywords in the biochar catalyst research field. In part a, the size of the node represents the frequency of the keyword. The closer the central color of the node is to red, the earlier the word was first used.

cited journal (Table S1 and Fig. S3). Co-citation analysis indicated the top 10 publications that have contributed to research in this field (Table S2). Author collaboration network analysis indicated that the most important pioneers of biochar-catalyzed waste conversion investigations were A. Demirbas and Y. Wang (Fig. S2b and Table S3). The results provide information about the development of and future trends in biochar-catalyzed waste conversion research, which will be useful to researchers trying to understand this research field.

4.2.2. *Analyses of trends in category, keyword, and cluster co-occurrence in the biochar-catalyzed waste conversion research field*

4.2.2.1. Co-occurring categories. Co-occurrence analysis distributions for 78 topic categories in the biochar-catalyzed waste conversion research field were assessed to identify hotspots and trends. Summary statistics for the 10 most frequently co-occurring categories and their centrality values indicated that biochar-catalyzed organic waste transformation research is a multidisciplinary field relevant to various subjects, including Engineering, Chemistry, Energy & Fuels, Materials Science, and Green & Sustainable Science & Technology, as shown in Fig. 7(a) and (b). Engineering and Chemistry were the two most frequent subjects. This indicates that catalytic conversion processes and engineering regulations are of great interest in this research field. There is also great interest in the energy conversion processes involved in biochar-catalyzed waste conversion.

4.2.2.2. Keyword co-occurrence trends and citation burst analysis. Co-occurrence analysis of keywords related to polymer and waste feedstock conversion by biochar catalysts was carried out using CiteSpace to identify biochar catalyst research hotspots (Fig. 8(a)). The frequencies and centrality values of the top 20 academic keywords are shown in Table S4. The annual frequencies of these 20 terms are shown in Fig. 8 (b). “Biomass” was the most common keyword (Table S4), with a frequency of 193, followed by “biochar” and “pyrolysis”. These three keywords are for the basic materials and methods used to study polymer and waste feedstock conversion by biochar catalysts. Biochar has many sources (e.g., wood, straw, shells, manure, and sludge), and biochar applications are focused on adsorption of pollutants, so conversion of polymers and waste materials into functional materials by biochar to prevent environmental pollution has attracted much attention. As shown in Table S4, the highest centrality values were found for the terms “biomass” and “adsorption” (the centrality value was 0.18 for both terms). The ability of the photocatalyst to adsorb the target pollutant is an important factor affecting how effective catalytic degradation will be. Studies of substrate materials and adsorption in the field of polymer and waste material conversion into functional materials by biochar catalysts have therefore been important. Biomass is widely used as a carrier because of its excellent adsorption capacity, unique surface properties, readily modified functional groups, good electrical conductivity, chemical stability, loose and porous structure, high SSA, and large numbers of phenolic, hydroxyl, carboxyl, amino, and other functional surfaces groups on its surfaces. Biochar photocatalysts can rapidly adsorb organic pollutants from water and transfer the pollutants to catalytic sites, increasing the probability of organic pollutants and intermediates coming into contact with the photocatalysts. Biochar photocatalysts can cause large amounts of strong oxidizing substances to be produced when light is applied. This is conducive to organic pollutant mineralization in a water body. The good electrical conductivity of biochar can inhibit carrier compounding, meaning the carrier effectively prevents pollutants from agglomerating.

“Cellulose” and “conversion” had the second and third highest centrality values. 0.13 and 0.11, respectively. Chen et al. [95] found that cellulose is an important precursor for the catalytic conversion of biomass into functional materials by biochar catalysts. Cellulose, hemicellulose, and lignin have been pyrolyzed to investigate the pyrolysis process, kinetics, and volatile compound evolution and to characterize the products. Pyrolytic dehydration of cellulose allows cross-linking reactions to occur, which can eventually lead to coke forming. More liquid products form as the cellulose pyrolysis temperature increases, and the maximum bio-oil yield occurs at ~500 °C. A keyword development trend graph can be used to monitor transitions in a research field to some extent [88]. The overall trend for 1999–2023 indicated that the 20 keywords were hardly used before 2010 but were used increasingly after 2010 and the number of keywords then increased dramatically (Fig. 8(b)). We analyzed keyword frequency for 2020–2022 and found that the more frequent keywords were likely to indicate future directions in research into polymer and waste material conversion into functional materials using biochar as a catalyst. The three keywords with the highest cumulative frequencies between 2020 and 2022 were “biomass”, “biochar”, and “conversion”. Different polymers require different catalyst substrates, and there are no marked differences between the structures and adsorption properties of biochar derivatives and biochar, so biomass is the most popular choice for preparing photocatalysts. Using biomass to prepare photocatalysts to convert polymers into functional materials has therefore been a key research direction in recent years.

Similar results were given by citation burst analysis (Table 3, in which the duration of each cited outbreak is shown in bold). The keywords were divided into four groups. The first group contained some basic keywords for strong biochar photocatalysts such as “biomass”, “cellulose”, “activated sludge”, and “food waste”. The keywords in the second group were mainly related to functional material conversion methods (“catalytic conversion”, “pyrolysis”, “co pyrolysis”, and “co-

Table 3
Keywords citation burst analysis results.

Keywords	Strength	Begin	End	2000 – 2023
Biomass gasification	1.59	**2002**	2015	
Catalysis	1.78	**2007**	2009	
Biofuel	1	**2007**	2009	
Bio-oil	1.46	**2009**	2014	
Biopolymer	1.29	**2009**	2011	
Cellulose	2.78	**2010**	2015	
Biomaterial	1.31	**2010**	2011	
Catalytic conversion	2.01	**2011**	2015	
Pyrolysis	2.36	**2012**	2014	
Wood	2.11	**2012**	2015	
Mechanical property	1.18	**2013**	2014	
Activated sludge	0.91	**2013**	2015	
Catalyst	1.79	**2014**	2016	
Steam gasification	1.11	**2015**	2017	
Co-pyrolysis	2.65	**2016**	2018	
Mixture	3.03	**2017**	2018	
Graphene oxide	1.39	**2017**	2019	
Physical property	2.07	**2018**	2019	
Carbonization	2.06	**2018**	2019	
Food waste	2.57	**2019**	2021	
Biomass pyrolysis	2.33	**2019**	2021	
Polymer	1.39	**2019**	2020	
Hydrochar	2.37	**2020**	2021	
Waste plastics	2.07	**2020**	2023	
Biodiesel	1.67	**2020**	2021	
Catalytic fast Pyrolysis	0.99	**2020**	2021	
Biochar catalyst	1.79	**2021**	2023	
Biodegradable	1.1	**2021**	2023	
Hemicellulose	0.76	**2021**	2023	
Lignin	0.75	**2021**	2023	

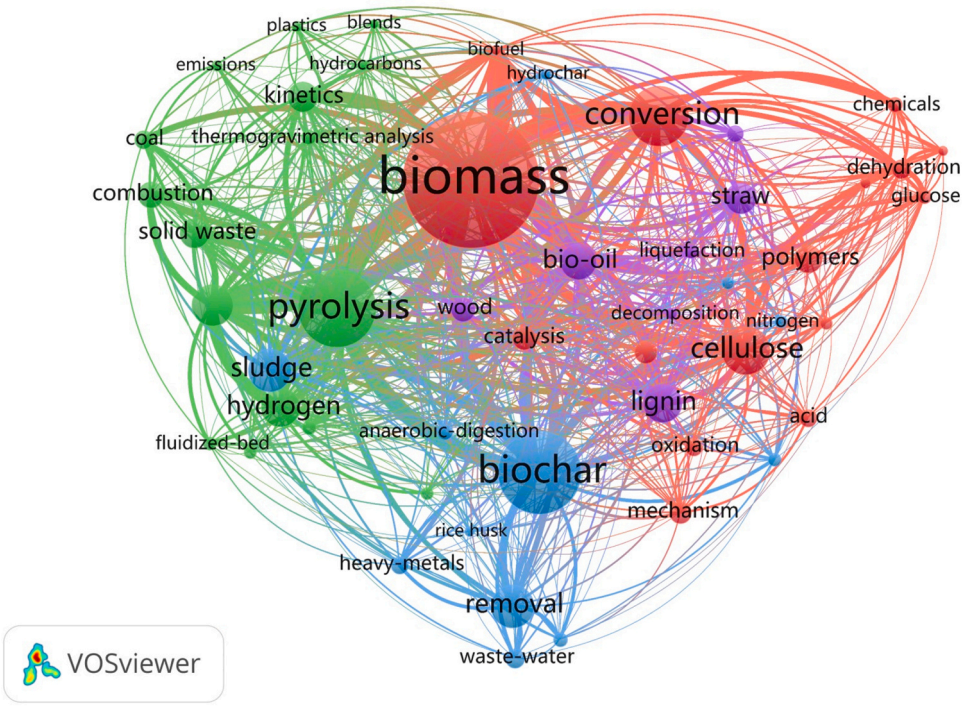

Fig. 9. Co-Co-occurrences of keywords in published research into polymer and waste-derived feedstock conversion into functional materials using biochar catalysts.

pyrolysis"). The third group, "mechanical properties", related to the reaction mechanism involved in the catalytic conversion process. The fourth group of keywords was mainly related to the products of biochar catalysis, such as "bio-oil" and "biopolymer". The results for keywords such as "catalysis", "catalytic conversion", "catalyst", and "biochar catalyst" indicated that there was continual research related to catalysis during the study period. The two keywords co-occurrence and citation burst analysis results indicated that researchers continue to investigate feedstocks for pyrolysis to produce biochar from the perspective of green and sustainable development and are constantly optimizing the pyrolysis conditions to use more feedstocks and produce more target products. The results for biochar and biomass indicated that modified conditions for preparing useful and long-lasting biochar catalysts are constantly being sought. Keyword co-occurrence analysis indicated that biochar-catalyzed polymer and waste conversion into functional materials is a current research focus and may remain an important focus of future research because of the practical importance of converting polymers and waste into functional materials.

4.2.2.3. Keyword cluster analysis. Keyword clustering analysis, performed using CiteSpace, classified all relevant keywords and identified logical relationships between keywords to allow the frontiers of the research field to be assessed and the research hotspots to be identified. In keyword clustering analysis, the profile value for a cluster indicates the credibility of the cluster. A cluster profile value > 0.5 indicates that the data are credible and a cluster profile value > 0.7 indicates that the data are convincing. The keyword clustering analysis map and the results after collating the clustering information are shown in Fig. S4 and Table S5, respectively.

Cluster #0, the largest cluster, contained 54 keywords and had a silhouette value of 0.728. Cluster #0 was labeled "pine wood" because pine wood or materials associated with pine wood have been the dominant raw materials used to produce biochar catalysts in recent years. Biochar catalysts were found to be central to the whole clustering network. Cluster #1 was labeled "fly ash" and contained 50 members and had a profile value of 0.785. Industrial plants produce large amounts of fly ash, lime, and other types of waste. Biochar catalysts can be used to transform such solid waste into functional materials and therefore allow sludge to be reused and the problems of disposing of solid waste to be solved, meaning transformation using biochar would be economically and environmentally beneficial [96]. Cluster #2, the third largest cluster, was labeled "combustion" and contained 49 members and had a profile value of 0.703. This cluster had a similar label to clusters #3 and #9 ("pyrolysis" and "co-pyrolysis", respectively, which are both methods of preparing biochar). Biochar is mainly produced from vegetation or fossil fuels decomposed at a high temperature to give a structurally stable carbon-rich porous material. The adsorption and catalytic properties of biochar are largely influenced by the type of feedstock and the thermochemical conditions used to produce the biochar [97]. Pyrolysis is an important method for cracking polymers such as plastics and also a common method for converting biochar catalysts and polymers into functional materials. "Combustion", "pyrolysis", and "co-pyrolysis" are therefore more common than other methods for converting functional materials and are of interest to researchers [98]. Cluster #5 was labeled "biodiesel" and contained 45 keywords and had a profile value of 0.837. Cluster #5 had the same properties as cluster #4 "hydrogel" and cluster #11 "tar", both of which are biochar catalysts generated from polymers that have been used in various fields. Cluster #7, "mechanical properties", indicated the intrinsic mechanisms involved in biochar catalyst reactions. Cluster #8, labeled "kinetics", indicated the kinetics of reactions between biochar catalysts and polymers and was used in relation to the biochar degradation rate. The mechanisms involved and the reaction kinetics are important features of biochar catalysts in relation to the surface area and structure of the biochar itself and the synthetic properties of the polymeric material being transformed. The mechanism and reaction kinetics determine the efficiency with which the functional material will be produced from a pollutant in a particular environment. The mechanisms and reaction kinetics of biochar catalysts need to be better understood to improve our ability to transform waste into functional materials. The conversion of polymers into functional materials using biochar catalysts will therefore need to be studied further in future. Cluster #10 appeared earliest, had the highest silhouette value of 0.983, contained 30 terms, and was labeled "palm kernel". From 20 years ago, when biochar started to be

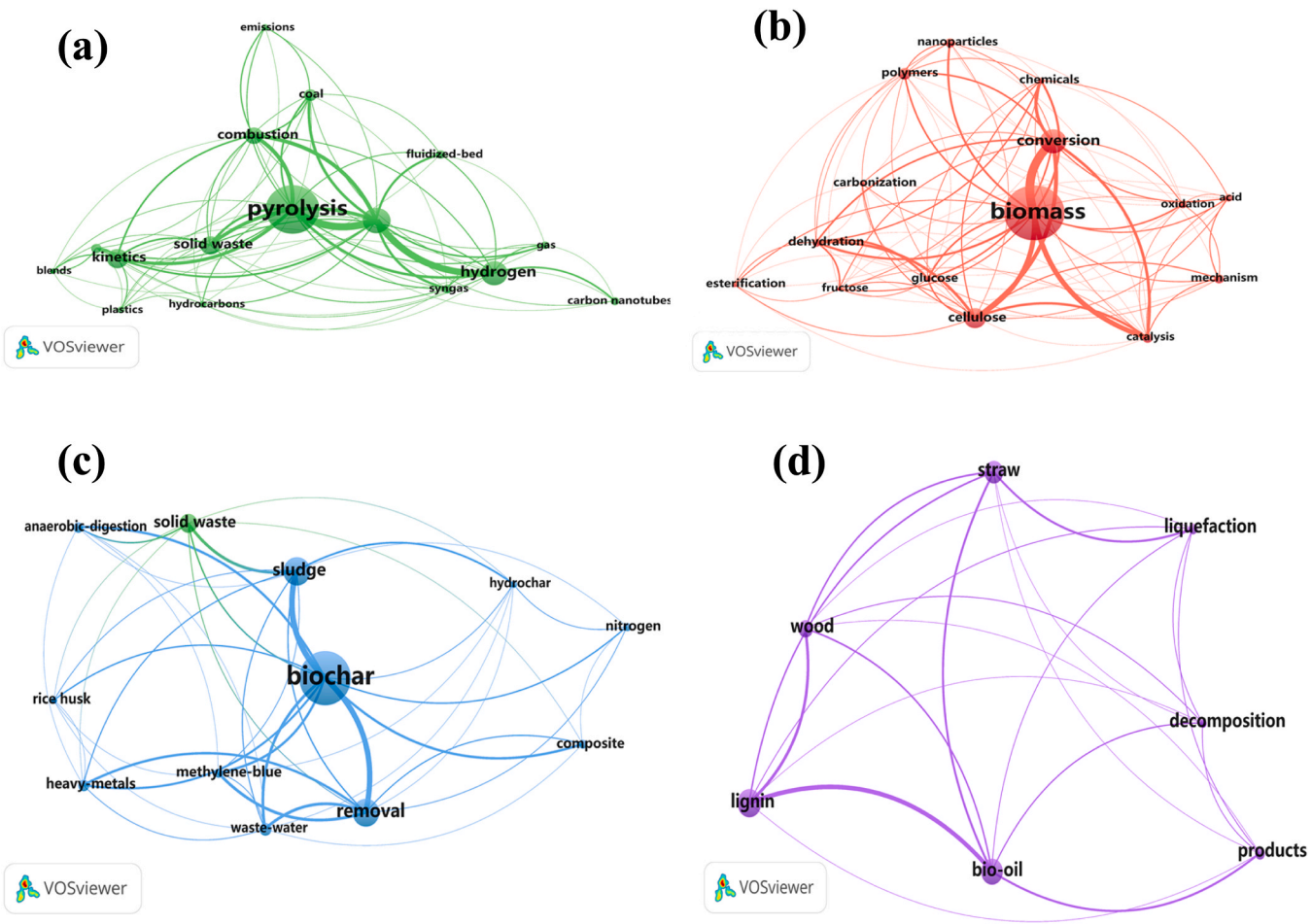

Fig. 10. (a) Research hotspot 1, (b) research hotspot 2, (c) research hotspot 3, and (d) research hotspot 4.

used as an adsorbent and catalyst, biochar was made from palm kernels more than any other raw material, and this was indicated by the keyword co-occurrence analysis results. Biochar can be made from a wide range of cheap materials such as wood, manure, and sludge, so biochar catalysts are cheap and readily prepared and can be transformed into organic materials to improve the overall performance. Composite materials can be transformed using organic matter in certain ways to improve the overall performance and efficiency.

4.2.3. Keyword co-occurrence graphs prepared using VOSviewer

Keyword co-occurrence analysis is the most direct and effective method for summarizing research trends in a specific field to help researchers quickly identify research trends. High-frequency vocabulary was used to identify research hotspots and map knowledge in the research field (e.g., "biochar catalysis") to indicate attention researchers are paying to areas outside specific topics. A visual representation of a network containing 51 keywords with each keyword appearing at least 10 times is shown in Fig. 9. In the figure, "biomass" has the highest total link intensity because of the abundance of biomass sources such as sludge and rice husks in municipal solid waste. Biochar is produced from these sources through dewatering, high-temperature pyrolysis with combustion of gaseous products, and other transformations. "Pyrolysis" (441 uses), "biochar" (389 uses), "conversion" (310 uses), "gasification" (208 uses), "bio-oil" (205 uses), and "hydrogen" (165 uses) are other highly relevant keywords that appeared frequently and are closely related to the research field. The keywords were grouped into four categories based on their co-occurrences, and each category was represented by a different color. These categories indicated four research hotspots and therefore clearly indicated directions in each research area.

(1) Research hotspot 1

As shown in Fig. 10(a), the study was focused on analysis of gases and products emitted from waste plastic or solid waste during gasification or pyrolysis. Conversion into gases through gasification or pyrolysis in the presence of a catalyst was a hotspot. The other modules indicated that the catalyst was generally biomass or biochar. The cluster of nodal terms with high weightings included pyrolysis, combustion, gasification, solid waste (sludge, urban solid waste, and other terms), and hydrogen. This cluster highlighted the efforts of researchers to determine the optimal parameters for effectively converting waste into syngas or various gases through pyrolysis, gasification, and other processes to produce usable substances with strong kinetic performances. Using solid waste or plastic as a catalyst during pyrolysis can require a large amount of energy and give low-quality products. However, the pyrolytic conversion rate of a biochar catalyst can be increased by decreasing the pyrolysis temperature, increasing the conversion time, and removing pollutants through adsorption. These improvements can increase the yield and offer better selectivity of liquid and gaseous products and therefore ultimately enhance the production of the desired functional materials. Combining solid waste and waste plastic pyrolysis in the development and application of biochar catalysts is therefore a key research direction [99].

Organic solid waste such as sludge, municipal solid waste, coal, and plastics (particularly polyethylene and polyvinyl chloride) with mesoporous, microporous, or layered structures are excellent catalysts of pyrolysis. Cracking, cyclization, oligomerization, isomerization, and aromatization reactions are enhanced by biochar catalysts and have been used to produce high-quality gas and liquid products. The SSA and

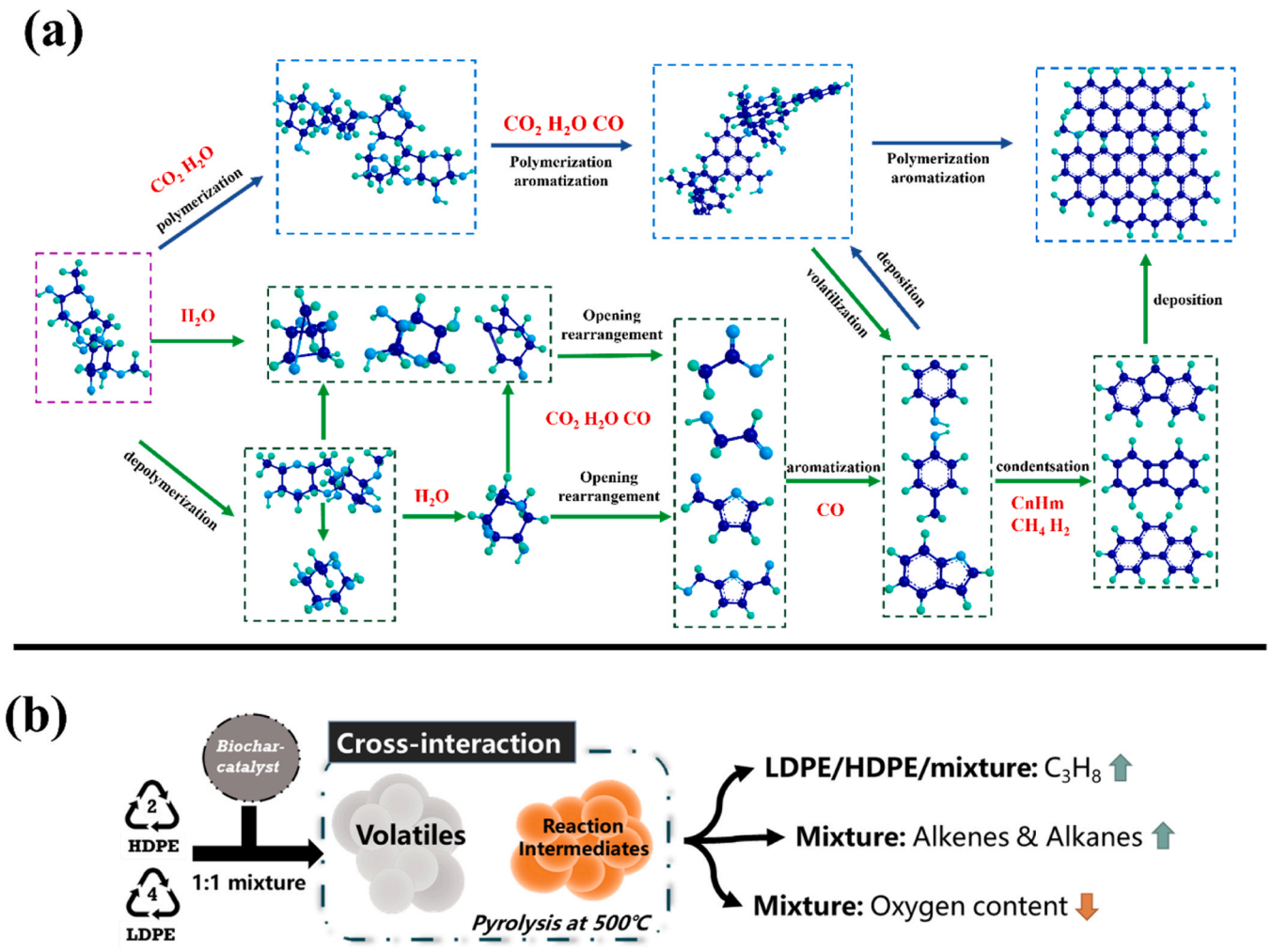

Fig. 11. (a) Pyrolytic reaction pathways for cellulose. (b) Reactions of polyethylene during pyrolysis with biochar catalyst.

porosity are the two main factors that affect the catalytic conversion capacity of biochar. Increasing the SSA and porosity of biochar improves the yield and quality of gas or liquid products of organic solid waste [100]. Hussain et al. [101] optimized the pyrolysis conditions by performing tests using different temperatures, amounts of catalyst, and reaction times. Catalytic thermal cracking using white cement catalysts and brick powder catalysts under optimal conditions to pyrolyze polystyrene increased the yield and improved the liquid and gaseous product quality [101]. Gasification of coal or solid waste can improve the efficiency of the reaction and the quality of the gas because of the kinetics of the reaction. However, coke formation on the catalyst surface during pyrolysis or cracking of solid waste or plastic can prevent the reactants reaching the active sites and pores in the catalyst and therefore cause catalyst failure. Further research is needed to develop appropriate strategies for extending the lives of catalysts used in pyrolysis and gasification processes for converting municipal solid waste and plastic considering the economic feasibility of such reactions and the potential for generating multiple products.

(2) Research hotspot 2

The second keyword in Fig. 10(b) indicates polymer conversion using biomass catalysts and the products of such reactions. “Biomass” was the largest node in this cluster, indicating the method used by researchers to convert polymers and waste-derived feedstock into functional materials using biochar catalysts and the main factors affecting the production of functional materials. Biochar is produced from biomass in an oxygen-limited atmosphere via thermochemical decomposition of carbon-rich substances. Biochar has a large surface area, is stable [102], effectively adsorbs heavy metals, small organic molecules, and ions [103], and contains lignin, cellulose, chitosan, activated carbon, and fly ash. Biochar can be used during pyrolysis to convert polymers and waste-derived materials into functional materials (Fig. 11(a)). The forms and products of biochar catalysts for converting polymers and waste-derived raw materials into functional materials were investigated by using VOSviewer to generate a density visualization map based on the 676 articles in our dataset. Transformation, dehydration, esterification, carbonization, catalysis, and hydrolysis were included, and it was noteworthy that catalysis (656) and hydrolysis (1847) strongly correlated. We could therefore analyze two key trends shown by the data. Studies of methods for converting polymers or waste-derived raw materials into functional materials using biochar catalysts were published by a large number of authors. This implied that initial relevant information about biochar or biomass catalysts was recently used by other researchers interested in converting polymers into functional materials. Limitations on converting polymers or waste-derived feedstocks into functional materials using biochar catalysts have been progressively overcome. Biochar catalysts for converting polymers and waste-derived raw materials into functional materials give different products, such as glucose, fuels, biodiesel, oil, and acids, which can be used in various applications and are therefore

described in publications in the energy research field and other related fields [104].

(3) Research hotspot 3

The third central word (Fig. 10(c)) indicated the use of biochar and sludge to remove pollutants. This involves using solid waste (sludge) and rice husks calcined in N_2 to create biochar, which can then be combined with other materials to give complex functional materials, including carbon nanomaterials. These materials can effectively remove pollutants such as methylene blue and heavy metals from acidic wastewater. VOSviewer indicated that solid waste was repeatedly mentioned in publications, suggesting that it can be used to catalyze the production of gaseous compounds through thermal contact or can be transformed into biochar and calcined to remove pollutants. The results indicated that functional materials can be used to remove heavy metals and dyes from acidic wastewater or other wastewater through catalytic mechanisms or oxidation. Decreasing the production costs of gas products and decreasing the amounts of solid waste needing to be disposed of can alleviate some burdens on society. Wastewater treatment plants produce sludge, which can be repurposed to produce useful materials. However, the limited amounts of fly ash and bottom ash that are available will limit the usefulness of applying the method to fly ash and bottom ash [105]. We concluded that sludge can be converted into functional materials to alleviate the environmental burden to some extent and that this is a cheap and efficient way of decreasing the costs and time required to treat sewage.

(4) Research hotspot 4

The fourth research hotspot (Fig. 10(d)) was found to be the use of biomass as a carrier of catalysts for removing pollutants and producing biomass oil. This approach can both degrade pollutants and recover products. Increasing research has been performed on pollution control and other fields in recent years, and biochar has increasingly been attracting attention in the environmental remediation field because of its unique physical and chemical properties and good adsorption properties. The central word for cluster 4 was “lignin”, which was also a searched keyword. The structural and physical properties of activated carbon [106] and biochar [28] produced from lignocellulosic mean these materials can be used in various applications and particularly to degrade pollutants during conversion into functional materials. For example, Li et al. pyrolyzed low-density polyethylene/high-density polyethylene blends with a biochar catalyst synthesized through gasification of poplar wood (Fig. 11(b)). This biochar facilitated catalytic pyrolysis of low-density polyethylene, and volatile compounds that were produced were efficiently cracked over the biochar catalyst to give more products [28]. However, heavy tar and wax were produced during the catalytic pyrolysis of high-density polyethylene because pyrolysis of high-density polyethylene involves biochar-catalyzed polymerization rather than catalytic cracking of recombinants, and this will cause changes in the crystallinity, surface functional groups, and internal structure of the biochar [107]. Catalytic pyrolysis reactions have been found to be affected by the acidity, SSA, and pore distribution of the catalyst [108]. Li et al. [28] suggested that the spent biochar used had a high degree of crystallinity and little effect on temperature-programmed oxidation. As the reaction progresses over time, a higher temperature is required to oxidize the biochar. Thermogravimetric analysis was performed, and lower mass loss rates were found for spent catalysts than new catalysts. The production of biomass oil from fresh and spent biochar suggests that the non-fixed structure of biochar become partly degraded through being involved in thermal decomposition of plastic. It is therefore necessary to carefully determine the structures of biochar catalysts during degradation and product generation.

5. Integrated prospects for biochar: computations, applications, and sustainability

On top of the detailed information about biochar catalysts, an explicit viewpoint with the aid of computational approach using biochar, biochar applications, and the role of biochar in improving sustainability are presented here. The catalytic mechanisms involved in biochar have been well established through experimental studies conducted previously. Biochar uses could be developed more quickly than was previously possible using computational techniques and artificial intelligence to model and optimize systems. Biochar with specific desired properties could be prepared (as summarized by Weber and Quicker [109]) with the help of computational techniques applied to the different preparation stages, from biomass source selection to application. Various models targeting different research areas are well established. For example, there is a deterministic agricultural production systems simulator model (a complex parameter aggregated simulation for studying the effects of biochar on different soil and crops [110]), a numerical model with substantial heuristic assumptions for describing heat and mass transfer between soil and biochar [111], a theoretical simulation of a three-site model to reflect the true acid–base behaviors of biochar [112], and an experimental coupled model of adsorption kinetics for modified sawdust biochar [113]. Another interesting research area is targeting data-oriented biochar design based on large numbers of publications with the aim of (1) reverse engineering [114] to select the most appropriate biomass and pyrolysis temperature and (2) determining the ability of biochar to adsorb pharmaceuticals [115]. Leng et al. [116] published a comprehensive review of biochar stability determined using the mean residence time calculated using an *n*-pool model ($n = 1,2, \ldots, N$), global warming potential for 100 years, and its relative half-life. Several studies were also investigated at a major spectrum which discussed: (1) the water saving with soil biochar amendment in United States [117], (2) pragmatic consideration on economic feasibility with social perspective of biochar in China [118], and (3) interpretation of effect on soil hydrological properties and crop water usage efficiency [119] based on a meta-data obtained globally. Various studies of biochar improvements achieved by optimizing the preparation process using algorithms such as response surface methodology [120], Taguchi-design [121], fractional factorial-based desirability function optimization [122], the Box–Wilson model [123], and NSGA-II [124] have been performed. The optimal conditions for recovering phosphorus using algae-derived biochar were identified and a cost–effect analysis was performed using a two-film model [125]. Apart from experimental-related research that involves optimization, a discussion at wider spectrum of biochar in terms of elevating biochar production and its evitable role in carbon management networks were made [126]. A mixed-integer linear programming model of biochar carbon management networks from the source–sink viewpoint has been developed [127] and expanded to consider economic aspects in terms of profitability optimized using two objective functions [128].

The use of artificial intelligence to investigate biochar has led to promising improvements in a wide area, from improving our understanding of the properties of biochar to improving biochar production processes by optimizing the process parameters. Various machine learning algorithms such as extreme gradient boosting [129], the leave-one-out cross-validation polynomial regression model [130], gradient boosting algorithms, and random forest algorithms [131] have been used to predict biochar yields. The machine learning approach has also been used to improve heavy metal (Pb and Cd) adsorption. This has been achieved using (1) a back-propagation neural network [132], (2) a Kernel extreme learning machine and Kriging model [133], (3) an artificial neural network and random forest method [134], and (4) a combinatorial approach including 20 different machine learning models (including support vector machine, RF, artificial neural network, M5Tree, and Gaussian process models) [135]. The biochar yield was predicted by coupling an optimization algorithm (genetic algorithm and

Table 4
Summary of computational approach in the biochar-related research covering modeling, optimization, AI-related, and advanced.

Methods	Targets	Substrates (Biochar type)	Outcome	Ref.
Part A: Generic approach				
Agricultural Production Systems sIMulator (APSIM)	Biochar effects on crop productivity and soil quality	Woodchip biochar & hypothetical biochar (sensitivity analysis purpose)	This model successfully demonstrated the biochar effects on soils & crop yield	[110]
Numerical modeling	Study the heat and mass transfer between biochar and sandy soil	Pine (*Pinus sylvestris var. mongolica Litv*) and Poplar (*Populus davidiana*)	Developed one-dimensional numerical model to obtain water content distribution to establish importance of water equilibrium between biochar and sandy soil.	[111]
Theoretical simulation	Performing three-site model to study biochar acid-base behavior	*Spartina alterniflora* and *Eichhornia crassipes*	Thorough understanding which described distribution, concentration, and strength of acidic/basic site biochar is attained.	[112]
Experimental supported modeling	Study the adsorption kinetics of modified biochar towards removal of Cu (II) and tetracycline (TET)	Sawdust biochar which further doped with iron and zinc (Fe/Zn-biochar)	Experimental results were validated with six different adsorption kinetic models including: pseudo-first order, pseudo-second order, Elovich, two-compartment first order, intra-particle diffusion, and liquid film diffusion	[113]
Metadata-based reverse engineering	Develop model that could suggest feasible starting biomass and peak pyrolysis temperature	A total of 120 different biochar samples is considered	Generalized Linear Model is developed which described combinatorial effect on various biomass feedstock and peak pyrolysis temperature	[114]
Economic modeling	Determine economic feasibility with social perspective of biochar in China	Rice, maize, beans, wheat-based biochar	Identified the potentiality of producing biochar across several provinces in China as vast amount is undergone direct burning.	[117]
	Identify water saving with soil biochar amendment in United States	Woody, straw, shell, grass-based biochar	US regions is beneficial from biochar use, especially high sand content location.	[118]
Structural equation model with meta-analysis	Study impact of biochar on soil hydrological properties and crop water usage efficiency	Crop-residue, woody-based	A proven approach which biochar could improve soil hydrology and crop yield through biochar amendment.	[119]
Part B: Optimization				
Response surface methodology, RSM	Studying the effect of pyrolysis temperature on the physical and chemical properties of biochar produced from biomass	Rice-husk	Fuel ratio of the biochar made is reported as an alternative of fossil fuel with cleaner and economical viable option.	[120]
Taguchi-design	Investigate influence of various factors (i.e., temperature, activation time) for activating biochar	Food waste and agricultural crop residue (canola and oat hull)	Complete dye adsorption is found with the sample of food waste biochar and canola hull biochar suggested by RSM.	[121]
Fractional factorial-based desirability function optimization	Screening factors that are influencing the most to biochar yield	Sugarcane bagasse	Maximum yield of 44.6% is obtained at 720 W after 20 mins.	[122]
Box-Wilson model	Compare the biochar sample among various experimental parameter	Rice straw	Ideal production condition is identified among the temperature (500–600 °C) and heating duration (80–100 mins)	[123]
NSGA-II	Propose a multi-objective optimization function targeting higher heating value (HHV) and power consumption for ideal pretreatment of solid biomass.	Spent coffee grounds, Basic component biomass (hemicelluloses, cellulose, and lignin), Corn core (extract xylan)	Energy production of biochar is reduced significantly with 20.042 MJ kg^{-1} based on the optimized condition of torrefaction temperature and time at 244 °C and 27 min; duration of 43 s	[124]
Process model developed on two-film theory	Optimal point identification of phosphorus recovery and the cost-effect for an algal-derived biochar developed	Sewage-derived algal biomass	Unit cost of leaching P is $5.23/kg P (recovering cost at $5.98/kg P) with series of ideal operating condition.	[125]
Mixed integer linear programming (solve with LINGO)	Develop multi-period source-sink network for the biochar in large scale	Not specified	Successfully develop of carbon management network for biochar which ensure purity level of biochar at large scale.	[127]
Bi-objective optimization	MILP model with bi-objective which maximizing CO_2 sequestration and annual profitability	Coconut shell, rice husk, bagasse	Ideal carbon management network for biochar which consider in terms of economic and environment.	[128]
Part C: Artificial Intelligence				
Linear regression, feed-forward neural network, deep neural network, Cubist, K-nearest neighbor, Random Forest	Determination of adsorption capability for biochar towards pharmaceutical components with machine learning model	Not specified (data from various publications, 88 different types of biochar)	Biochar's structure shall be focused instead of functional group; equilibrium adsorption performs best with Cubist with mean absolute error of 6.9 and R^2 of 0.98.	[115]
eXtreme Gradient Boosting	Develop robust machine learning model predict algal biochar with multiple input parameter	Algal biomass (59 microalgae, 19 macroalgae, 19 defatted algae, 8 algae residue)	High accuracy of algal biochar prediction with XGBoost model.	[129]
Leave-One-Out cross-validation polynomial regression model	Evaluate the effects of catalyst quantity and pre-treatment temperature on the product formation during pyrolysis of sawdust	Sawdust	Successful obtain of equation for different parameters polynomial regression performed on experimental value which further identified biochar yield (alongside with bio-oil and biogas).	[130]
Gradient boosting & Random Forest	Explore the relationship between the characteristics of biomass and biochar yield, surface area, and nitrogen content and further optimize pyrolysis parameter.	400 different biochar samples from 64 biomasses.	Provides insights into the relationship between biomass characteristics and biochar yield, surface area, and nitrogen content.	[131]
Back-propagation neural network	Develop a biochar heavy metal adsorption prediction model based on multiple linear	353 different biochar types	Sufficiently provides information on properties of biochar and its application in	[132]

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Table 4 (*continued*)

Methods	Targets	Substrates (Biochar type)	Outcome	Ref.
	regression (MLR) and to explore the effect of different parameters on heavy metal adsorption by biochar.		removing heavy metals from water environments.	
Kernel extreme learning machine & Kriging model	Investigate the effect of different parameters on the heavy metal adsorption capacity of biochar, and to identify the most sensitive parameters using local sensitivity analysis	44 different types of biochar	The content of total carbon plays a crucial role in determining the degree of porosity and specific surface area of biochar, and it is an essential factor in biochar experiments.	[133]
Artificial neural network (ANN) & Random Forest (RF)	Investigate the characteristics of biochars produced from lignocellulosic biomass by pyrolysis and to develop a predictive model for heavy metal adsorption efficiency based on measurable biochar characteristics	44 different types of biochar	Provide a comprehensive understanding of the removal of heavy metals using biochars and guidance for real wastewater and polluted groundwater containing heavy metals.	[134]
20 different machine learning models	Propose and evaluate predictive models for the sorption efficiency of heavy metals in biochar systems.	Not specified	Identified a potential issue with the input variables used in the models and recommended removing one of the variables to ensure the objectivity of the model.	[135]
[A] ML model: Ensemble Learning Tree (ELT), Gaussian Process Regression, Support Vector Machine, Decision Tree [B] Optimization: Particle Swarm optimization (PSO) and Genetic Algorithm	Propose an approach which optimize and predict the biomass pyrolysis process based on biomass properties (ultimate, proximate, and structural analysis) and pyrolysis reaction conditions (heating rate, temperature, particle size, time, and flow)	Not specified	Successful demonstration of various combination between ML and optimization in which ELT-PSO has best performance with least RMSE and high R^2.	[136]
Random Forest	Determine the critical factors that influence the removal of Cr(VI) by biochar and to identify the most effective biochar properties for this purpose	Corn Straw, Rice Husk, and Swine Manure	The biochar's specific surface area plays a crucial role in the removal of aqueous pollutants, and biochar with a well-developed pore structure is essential for this purpose.	[137]
Support Vector Machine, ANFIS, PSO-ANFIS, Genetic programming,	Investigate the adsorption capacity of biochar for heavy metals in water resources.	Agricultural waste and sewage sludge	Biochar has a high adsorption capacity for heavy metals, and the characteristics of biochar are influential factors in determining its adsorption capacity	[138]
Support Vector Regression (SVR), Neural Network (NN), RF	Develop a biochar-based remediation plan for heavy metal-contaminated soils	Not specified	Successfully identified an explicit insight on the immobilization efficiency of heavy metals in biochar-amended soils.	[139]
XGBoost, RF, Gradient Boosting Decision Tree	Implement tree-based machine learning to identify the ideal conditions and selectively alter the properties of biochar to achieve optimal methane yield and maximum methane production rate values in anaerobic digestion with different substrates.	Not specified	ML models can effectively support practical situations, save costs and time dedicated to research, and improve prediction efficiency relative to conventional experiments.	[140]
Random Forest	Investigate the most influential mechanisms of PPCPs (Pharmaceuticals and Personal Care Products) adsorption by biochar	Agricultural, forestry, food, and industrial type	The study showed that the models developed by detailed biochar properties, such as surface functionality and hierarchical porous structure, were more accurate in predicting the PPCPs adsorption capacity of biochar	[141]
XGBoost, RF, SVR, NN	Understand the link between various properties of biochar and the corresponding mechanisms promoting nonradicals	Not specified	High specific surface area and O% values can significantly enhance nonradical contribution in biochar catalysts	[142]
Part D: Advanced approaches				
Molecular dynamics	Investigate the properties of different biochar samples, specifically their adsorption capabilities, using various tests such as nitrogen adsorption, Raman spectroscopy, and XPS testing	Corn straws	Specific surface area and pore size distribution of four different biochar samples were analyzed through nitrogen adsorption tests using a BET method.	[143]
	Investigate the effectiveness of using biochar as a functional material for improving the aging resistance of bituminous composites and for capturing CO.	Woody biochar (pristine biochar) and algal biochar (IFC)	– Woody biochar improved the rheology-based and chemistry-based aging indexes of bituminous composites by 13% and 28%, respectively. – Algal biochar (exhibited much higher improvement of 45% and 35% in the respective indexes.	[144]
	Evaluate the effectiveness of different types of biochar as sorbents for removing micropollutants from water.	Coconut shells, Coconut husks, Rice straw, Corncobs	Identified the effectiveness of biochar as a sorbent for micropollutants depended on its source of raw material, pyrolysis temperature, and surface characteristics	[145]
	Investigate the crystallization kinetics of biochar modified bio-asphalt binders (BMBA) and to propose a model for the crystallization kinetics in terms of the numbers of crystal nuclei, nucleation rate, and crystallinity.	Wastewood	Successfully proposed a model for the crystallization kinetics of BMBA and found that the second crystallization process could be controlled or inhibited with the right biochar content	[146]
QSAR	Optimize and simulate the 3D structures of biochars using molecular simulation methods and quantum chemistry in order to better understand their structures and properties	Crop straw-derived	- Elemental analysis and spectroscopic techniques is used to analyze the molecular structures of biochars and build 2D models - Experimental elemental concentrations and chemical functional groups were compared	[147]

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Table 4 (*continued*)

Methods	Targets	Substrates (Biochar type)	Outcome	Ref.
			with the simulated ones to confirm the availability of 2D models	
	Discusses the synthesis and characterization of cobalt-doped shrimp shell biochar for the degradation of organic pollutants in wastewater	Shrimp shell powder	- Pyrolysis temperature has a significant effect on the morphology and structure of biochar. - Biochar produced at a relatively high calcine temperature has increased surface area and porosity, which effectively degrades organic pollutants. - Cobalt-doped biochar is a promising catalyst for the degradation of organic pollutants in wastewater.	[148]
	Investigate the effects of biochar amendment on the soil microbial community and the growth of lettuce plants in soil contaminated with the antibiotic oxytetracycline	Corn straw	- Biochar amendment also significantly increased the concentration of available nitrogen and phosphorus in the soil. - The biochar-amended soil also had significantly higher levels of oxytetracycline degradation compared to the control soil. - Growth of lettuce plants was significantly improved in the biochar-amended soil.	[149]
	Implement QSAR model which predict removal efficiency of sulfonamide antibiotics with iron-impregnated biochar	Corn straw	Removal efficiency of 14 sulfonamide antibiotics is successfully investigated	[150]
DFT	Investigate the properties and adsorption performance of biochar models doped with different atoms and to determine their potential for greenhouse gas (GHG) capture.	Seaweed based biochar	The adsorption energy data from the study suggests that and can be more accurately used as a viable descriptor for the initial screening of biochar material models with high adsorption energy for GHG.	[151]
	Investigate the microcosmic interaction between rhenium oxide (ReO) and different acidic and basic oxygen-containing groups (hydroxyl, carboxyl, pyrone and chromene) on biochar.	Not specified	The DFT calculations indicated that the adsorption of oxygen-containing group functionalized BC towards ReO was gradually strengthened as the pH decreased.	[152]
	Produce mesoporous cellulose biochar (MCB) adsorbents with different surface area, morphology, and functionalities content, and evaluate and compare their Cd(II) adsorption performance	Cellulose biochar	MCB adsorbents showed high Cd(II) adsorption capacity, and the adsorption performance was found to be influenced by the surface area, morphology, and functionalities content of the adsorbents.	[153]
	Prepare N-doped biochar loaded by FeS (FeS@NBC) and comprehensively characterize its morphological properties	Corn straw	FeS@NBC/PS system showed excellent adsorption and degradation performance towards phenol, with a degradation efficiency of 92.7% observed.	[154]

particle swarm optimization) with several machine learning algorithms by Haq et al. [136]. Artificial intelligence has been used to identify biochar applications in the fields of engineered biochar [137], industrial wastewater [138], heavy metal immobilization in soil [139], anaerobic digestion [140], adsorption of pharmaceuticals and personal care products [141], and water remediation [142]. In the event which detailed understanding of biochar design is intended, molecular dynamic simulations can provide insights into the pore structure, surface functional groups, and thermal stability. There are numerous publications relating to biochar functionalities such as (1) adsorption of phenol [143], (2) the effects of different types of biochar on aging [144] of bituminous composites [145], (3) micropollutant removal efficiencies during water treatment [146], and (4) biochar crystallization kinetics [147]. Zhao et al. built a three-dimensional conceptual biochar model with a molecular dynamic simulation to study relative quantitative structure–activity relationships [148]. Quantitative structure–activity relationship models have been used to identify potential environmental effects of using biochar from the physicochemical properties of the biochar, and such studies have been focused on peroxymonosulfate activation by cobalt-doped biochar [149] and urea–hydrogen peroxide activation by MgFe-layered double hydroxide engineered biochar [150] and iron-impregnated biochar [151]. The properties of biochar have been investigated in detail using density functional theory using the Schrödinger equation and calculations from first principles [152]. Biochar-related research using density functional theory has been performed to investigate (1) the ability of biochar materials to adsorb greenhouse gases [153], perrhenate [154], Cd (II), and Cr (VI) [155] and (2) phenol reaction paths and reaction sites [54].

Biochar has been used widely in various industries because it is environmentally benign and can be produced from natural resources. Woolf et al. [156] found that biochar can be used to mitigate the effects of chemicals with strong climate change potentials and to give other benefits such as providing energy and improving crop growth. These claims were supported by Paustian et al. [157], who compared various methods for mitigating agricultural emissions of greenhouse gases and found that biochar has a relative strong ability to sequester carbon in soil and could be used on large areas of land. Kalinke et al. [158] identified electrochemical applications of biochar such as in batteries [159], supercapacitors [160], fuel cells [161], and hydrogen storage and oxygen electrocatalysis systems [162]. Biochar has remarkable potential for the use treating wastewater [163], controlling air pollution [164], in cement composites [165], and in the steel industry [166]. Systematic assessments of the environmental effects of biochar need to be performed, as noted by Terlouw et al., by performing thorough lifecycle assessments for biochar and other CO_2-removal techniques. Downie et al. [167] published explicit insights into managing the risks posed by biochar. A summary of all the computational approaches that have been used is presented in Table 4, which contains four parts (part A: generic approaches, part B: optimization, part C: artificial intelligence, and part D: advanced approaches). However, there are no comprehensive study on the impact of biochar towards a firm linkage on sustainability which covering different aspects that is relatable to the concept of ESG (Environment, Social, and Governance) and could be aligned with the United Nations Sustainable Development Goals, SDGs. A summary of the sustainability concern of biochar towards ESG is layout in Table 5 which could be extended by parties involved with biochar by allowing to

Table 5
Sustainability role of biochar in terms of Environmental, Social, and Governance.

Environmental, E		Social, S		Governance, G	
Key aspects	Details	Key aspects	Details	Key aspects	Details
E1. Carbon sequestration	The stable carbon structure of biochar allows it to serve as a long-term carbon sink, playing a role in climate change mitigation efforts.	S1. Food security	Increased crop yields resulting from the use of biochar as a soil amendment contribute to global food security.	G1. Sustainable sourcing	Companies showcasing their commitment to sustainable sourcing practices and the circular economy can utilize biochar derived from waste biomass.
E2. Waste valorization	Converting waste biomass, such as agricultural residues and organic waste, into biochar helps reduce waste and supports a circular economy.	S2. Rural development	The production and application of biochar create new job opportunities in rural areas, fostering economic development and poverty reduction.	G2. Innovation and research	Commitment to innovation and sustainable technologies can be demonstrated by companies investing in research and development of biochar applications.
E3. Soil health	When used as a soil amendment, biochar can enhance soil fertility, water retention, and nutrient availability, promoting sustainable agriculture.	S3. Public health	Improving air and water quality through pollution control and water treatment with biochar benefits public health and well-being.	G3. Stakeholder engagement	Responsible governance can be showcased by companies engaging with stakeholders, such as local communities and regulators, in biochar projects.
E4. Pollution control	The ability of biochar to remove contaminants from air, water, and soil contributes to a cleaner environment and improved public health.	S4. Education and capacity building	The promotion and adoption of biochar technologies create opportunities for education and capacity building in local communities.	G4. Transparency and disclosure	Ensuring transparency and disclosure of information related to biochar sourcing, production, and application allows investors and customers to make informed decisions.
E5. Biodiversity and ecosystem conservation	Using biochar in soil remediation and land reclamation projects helps restore degraded ecosystems and promote biodiversity.	S5. Health and safety	Removing harmful contaminants from air, water, and soil with biochar improves health and safety for communities affected by pollution.	G5. Regulatory compliance	Compliance with all relevant regulations and standards related to biochar production, application, and trade is crucial for companies.
E6. Energy efficiency	Incorporating biochar-based materials, such as thermal insulation and lightweight construction materials, can improve energy efficiency in buildings.	S6. Cultural preservation	Employing biochar in traditional agricultural practices helps preserve cultural heritage and promotes the transmission of traditional knowledge.	G6. Ethical business practices	Ethical considerations should be taken into account by companies in their biochar-related activities, evaluating potential impacts on local communities, the environment, and global sustainability goals.
E7. Renewable energy	Biochar serves as a sustainable feedstock for the production of renewable energy, such as bioenergy, through gasification or anaerobic digestion.				

showcase the commitment to ESG principles which could persuade the decision maker and attracting investors or customers that concerned about overall sustainability.

6. Conclusions

Catalytic conversion of waste and waste reclamation and utilization are considered to be the most appropriate approaches to waste treatment. In this work, the current situation and trends in research into using biochar catalysts to treat solid waste were analyzed by performing bibliometric analyses. The principles underlying biochar catalysis of the transformations of various pollutants and the effects of the physicochemical properties of biochar on catalytic conversion activities and products were investigated. The main results are shown below.

(1) In situ transfer catalysis of waste is more effective than other methods. In situ transfer catalysis is more flexible, give better product selectivity, and is a simpler process but gives a lower conversion efficiency than in situ catalysis.
(2) The surface properties of biochar affect the reaction rate. Increasing the number of pores, SSA, surface charge, and number of functional groups increases the catalytic activity and reaction rate.
(3) Econometric studies indicated that relevant research into biochar-catalyzed waste conversion has been performed in many countries since 2006. This indicates that research into biochar-catalyzed waste conversion is a hot topic of ongoing interest around the world and deserves more in-depth research and analysis. There are more citations of publications in Bioresource Technology than in other journals.
(4) Biomass can be used as a catalyst carrier for converting and liquefying polymers and other forms of biomass. Carbon-rich materials adsorb heavy metals, small organic molecules, and ions during thermochemical decomposition and efficiently convert polymers and waste derivatives into functional materials through pyrolysis. Sludge can be transformed into functional materials, and this will decrease the burden of sludge on the environment.

7. Future research directions

We identified scientific challenges that have been relatively well addressed and scientific challenges that have not been sufficiently explored or remain to be addressed. Here, we suggest future research directions. (1) Different functional groups affect catalytic conversion reactions differently, but these different effects have not been systematically studied. Further research into the mechanisms involved in the roles of different functional groups in catalytic conversion reactions is needed. (2) Metals affect the SSA, porosity, and functional groups of biochar and also act as active sites during catalysis by biochar and modified biochar. Few studies of the effects of specific elements and metal–carrier interactions in biochar catalysts have been performed, so comprehensive and systematic studies should be performed. (3) Few studies of how different sources of biochar affect the surface charge have been performed, and there is great potential for further research into the surface charges of biochar with different sources in different environments. (4) Conversion of polymers by biochar catalysts into functional materials has limitations but should be studied in more depth.

Many biochar applications in other fields are possible, and many applications may yet be discovered. A good number of integrated

computationally aided studies involving modeling, optimization, machine learning, and advanced approaches have been performed. A number of successful studies related to biochar have been published, but it is worth mentioning barriers to biochar use around the world. The main barriers are great uncertainty in terms of (1) capital investment for scaling up and the potential for making a profit and (2) policies supporting biochar use and financial incentives for producing and using biochar, such as tax credits, loan guarantees, and subsidies for installing infrastructure. Addressing these issues could improve development of the biochar market by attracting more investors. Attention is being paid around the world to aligning business and sustainability, and the potential for biochar supporting environment, social, and governance practices needs to be assessed. Considering sustainability could steer development of the biochar sector toward the United Nations sustainable development goals (https://sdgs.un.org/2030agenda), to which many countries have responded by making commitments to aim for carbon neutrality by 2030. Proper analytical approaches targeting the techno-economic viability of using biochar as a catalyst should be used to promote various biochar applications rather than only for managing waste. Commercialization of biochar still has various hurdles (i.e., consistency of the feedstock characteristics, food security, and the biochar end application market) that need to be overcome before large-scale biochar production is possible. Sustainable biochar production requires environmental factors to be considered by performing lifecycle analyses to evaluate various environment impacts of biochar (i.e., global warming potential and land use). Social aspects such as job creation and acceptance by people living near biochar production sites are also key to achieving a sustainable biochar industry. Once these challenges are overcome, biochar may be used as a catalyst to achieve a sustainable circular bioeconomy.

CRediT authorship contribution statement

Honghong Lyu: Investigation, Data curation, Writing – original draft. **Juin Yau Lim:** Formal analysis, Visualization, Writing – original draft. **Qianru Zhang:** Writing – review & editing, Supervision, Funding acquisition. **Sachini Supunsala Senadheera:** Data curation, Resource, Data curation. **Chuchen Zhang:** Resource, Data curation. **Qilan Huang:** Visualization. **Yong Sik Ok:** Conceptualization, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

All data used in this study is stated in the manuscript.

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Appendix A. Supporting information

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